

# Triggering N<sub>2</sub> Uptake via Redox Induced Expulsion of Coordinated NH<sub>3</sub> and N<sub>2</sub> Silylation at Trigonal Bipyramidal Iron

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## Experimental Section.

**General Considerations.** All manipulations were carried out using standard Schlenk or glovebox techniques under a N<sub>2</sub> atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thoroughly sparging with Ar gas followed by passage through an activated alumina column in the solvent purification system by SG Water, USA LLC. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. HSiP<sup>Ph</sup><sub>3</sub>,<sup>i</sup> HSiP<sup>iPr</sup><sub>3</sub>,<sup>i</sup> and H(OEt)<sub>2</sub>[B(3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]<sup>ii,iii</sup> were prepared according to literature procedures. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Elemental analyses were performed by Columbia Analytical Services, Inc. (Desert Analytics/Transwest Geochem), Tucson, AZ or Midwest Microlab, LLC., Indianapolis, IN. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3-Å molecular sieves prior to use.

**X-ray Crystallography Procedures.** X-ray diffraction studies were carried out at the MIT Department of Chemistry X-Ray Diffraction Facility on a Bruker three-circle Platform diffractometer, equipped with a CCD detector. Data was collected at 100 K using Mo Kα (λ = 0.71073 Å) or Cu Kα (λ = 1.54178 Å) radiation and solved using SHELX version 6.14.<sup>iv</sup> X-ray quality crystals were grown as described in the experimental procedures. The crystals were mounted on a glass fiber or nylon loop with Paratone N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. N-H hydrogens were located on the Fourier difference map and allowed to refine freely in the cases of **6a**•B(ArF)<sub>4</sub>, **6b**•OTf,



**9a**, **9b**, and  $\text{N}_2\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3$ .

**Spectroscopic measurements.** Varian Mercury-300, Inova-500 and Brüker AVANCE-400 spectrometers were used to record  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{29}\text{Si}$ , and  $^{31}\text{P}$  NMR spectra at ambient temperature unless otherwise indicated.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were referenced to the residual solvent peaks.  $^{11}\text{B}$  chemical shifts were referenced to external boron trifluoride-diethyl etherate ( $\delta = 0$  ppm).  $^{15}\text{N}$  chemical shifts were referenced to external  $^{15}\text{N}$ -nitrobenzene ( $\delta = 370.4$  ppm).  $^{19}\text{F}$  chemical shifts were referenced to external hexafluorobenzene ( $\delta = -165$  ppm).  $^{29}\text{Si}$  chemical shifts were referenced to external tetramethylsilane, TMS ( $\delta = 0$  ppm).  $^{31}\text{P}$  chemical shifts were referenced to external phosphoric acid ( $\delta = 0$  ppm). Solution magnetic moments were determined by the method of Evans.<sup>v, vi</sup> Optical spectroscopy measurements were taken on a Cary 50 UV-Vis spectrophotometer using a 1-cm two-window quartz cell sealed with a standard closed cap purchased from Starna Cells, Inc (Catalog number: 1-Q-10-GL14-C). Infrared spectra were recorded on a BioRad FTS 3000 EXCALIBUR series FT-IR spectrometer. Agilent 5973N Gas Chromatograph/Mass Spectrometer was used for detecting aniline byproduct during the synthesis of  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{C}_6\text{H}_5)$  (**10**). **Electrochemistry.** Electrochemical measurements were carried out in a glovebox under a dinitrogen atmosphere in a one-compartment cell using a CH Instruments 600B electrochemical analyzer. A glassy carbon electrode was used as the working electrode and platinum wire was used as the auxiliary electrode. The reference electrode was  $\text{Ag}/\text{AgNO}_3$  in THF. The ferrocene couple  $\text{Fc}^+/\text{Fc}$  was used as an external reference. Solutions (THF) of electrolyte (0.3 M tetra-*n*-butylammonium hexafluorophosphate) and analyte were also prepared under an inert atmosphere. **DFT Calculations.** Single-point calculations on **5** and **12** were run on the

Gaussian03<sup>vii</sup> suite of programs with the RB3LYP level of theory with the 6-31++G\*\* basis set for all atoms.

**(SiP<sup>Ph</sup><sub>3</sub>)Fe(CH<sub>3</sub>) (1a).** HSiP<sup>Ph</sup><sub>3</sub> (2.43 g, 2.99 mmol) and ferrous chloride (0.379 g, 2.93 mmol) were combined in THF (100 mL) and cooled to −78 °C. CH<sub>3</sub>MgCl (2.1 mL of 3.0 M solution in THF, 6.3 mmol) was added dropwise with vigorous stirring for 20 min, causing an immediate darkening of the solution. The reaction mixture was slowly warmed to room temperature overnight, resulting in a dark red solution. The solution was introduced into the dry-box, 1,4-dioxane (15 mL) was added, and the mixture was stirred at room temperature for 2 hr. The solution was filtered through Celite and was concentrated to 10 mL. Red colored crystalline product was obtained from a benzene solution (20 mL) layered with pentane at room temperature. The resulting product (SiP<sup>Ph</sup><sub>3</sub>)Fe(CH<sub>3</sub>) (**1a**, 1.66 g, 1.88 mmol, 64%) was collected on a sintered glass frit, washed with additional portions of benzene, THF, and pentane and dried by vacuum. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 13.1, 5.5, 4.5, 3.8, 0.67, −5.5.  $\mu_{\text{eff}}$  (C<sub>6</sub>D<sub>6</sub>, 20°C): 2.84  $\mu_{\text{B}}$ . Red X-ray quality crystals were grown by diffusion of pentane vapors into a THF solution of **1a**; TBP ( $\tau = 0.91$ ).<sup>viii</sup> Anal. Calcd. For C<sub>55</sub>H<sub>45</sub>FeP<sub>3</sub>Si•1/2dioxane: C, 73.86; H, 5.33. Found: C, 73.85; H, 4.88. UV-Vis (THF, nm {cm<sup>−1</sup>M<sup>−1</sup>}): 314 {10,000}, 393 {8,100}. IR (KBr pellet; cm<sup>−1</sup>): 2902, 2856, 2785.

**(SiP<sup>iPr</sup><sub>3</sub>)Fe(CH<sub>3</sub>) (1b).** HSiP<sup>iPr</sup><sub>3</sub> (0.40 g, 0.657 mmol) and ferrous chloride (0.083 g, 0.655 mmol) were combined in THF (50 mL) and cooled to −78 °C. CH<sub>3</sub>MgCl (0.44 mL of 3.0 M solution in THF, 1.32 mmol) was added dropwise with vigorous stirring for 20

min, causing an immediate darkening of the solution. The reaction solution was slowly warmed to room temperature overnight, resulting in a clear red solution. The solution was introduced into the dry-box, 1,4-dioxane (10 mL) was added, and the mixture was stirred at room temperature for 2 hr. After adding pentane (30 mL) the resulting mixture was filtered through Celite and concentrated. Benzene (20 mL) was added and the resulting orange solution was filtered through Celite and dried under vacuum to give the product,  $(\text{SiP}^{\text{Pr}}_3)\text{Fe}(\text{CH}_3)$  (**1b**, 0.40 g, 0.589 mmol, 90%). Analytically pure material was obtained from crystallization from a concentrated pentane solution at  $-35\text{ }^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , ppm): 5.93, 5.47, 4.68, 0.22.  $^1\text{H-NMR}$  ( $\text{THF-d}_8$ , ppm): 6.0, 5.7, 4.6, 0.26.  $\mu_{\text{eff}}$  ( $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $2.80\ \mu_{\text{B}}$ . Crystals suitable for X-ray diffraction were obtained by slow evaporation of a pentane solution of **1b**; TBP ( $\tau = 0.96$ ). Anal. Calcd. For  $\text{C}_{37}\text{H}_{57}\text{FeP}_3\text{Si}\cdot\text{dioxane}$ : C, 64.22; H, 8.54. Found: C, 64.18; H, 8.35. UV-Vis ( $\text{THF}$ , nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 320  $\{5,000\}$ , 380  $\{4,100\}$ , 472  $\{1,500\}$ , 1,050  $\{170\}$ . IR (KBr pellet;  $\text{cm}^{-1}$ ): 2958, 2907, 2870, 2807.

$[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{THF})][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**2a**).  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{CH}_3)$  (0.200 g, 0.226 mmol) was dissolved in THF (20 mL) and cooled to  $-35\text{ }^\circ\text{C}$ .  $\text{H}(\text{OEt}_2)_2[\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (0.229 g, 0.226 mmol) was added and the solution was vigorously stirred for 1 hr at room temperature. After filtration through Celite the resulting dark red solution was concentrated to 5 mL. The product was obtained as a red powder by layering pentane over the solution and letting the solution stand overnight.  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{THF})][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**2a**, 0.361 g, 0.200 mmol, 88.5%) was collected on a sintered glass frit (M), washed with additional portions of pentane and dried by vacuum. The identity of the

product was established by comparison of its  $^1\text{H}$ -NMR spectrum with its published  $^1\text{H}$ -NMR spectral data.<sup>i</sup>

**$[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**3**).**  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{CH}_3)$  (0.500 g, 0.737 mmol) was dissolved in  $\text{C}_6\text{H}_6$  (50 mL) and cooled to  $-35\text{ }^\circ\text{C}$ . After adding  $\text{H}(\text{OEt}_2)_2[\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (0.746 g, 0.737 mmol) to the frozen solution, the solution mixture was vigorously stirred for 30 min at RT, resulting in precipitation of a blue solid. The precipitate was collected on a glass-frit (M) and washed with benzene (3 x 10 mL) and pentane (3 x 10 mL). The resulting blue-green powder,  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**3**, 1.06 g, 0.682 mmol, 92%), was dried under vacuum.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6/\text{THF-}d_8$ ; 5/1, ppm): 11.2, 8.2, 7.6, 6.5, 4,  $-4.9$ ,  $-7.5$ .  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6/\text{THF-}d_8$ , ppm):  $-61.1$  ppm.  $\mu_{\text{eff}}$  ( $\text{THF-}d_8$ ,  $20^\circ\text{C}$ ):  $3.3\ \mu_{\text{B}}$ . Blue X-ray quality crystals were grown by diffusion of pentane vapors into a THF solution of **3** at  $-35\text{ }^\circ\text{C}$ ; TBP ( $\tau = 0.99$ ). UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 420 {sh}, 500 {270}, 610 {145}, 755 {200} (See Figure S3). IR (KBr pellet;  $\text{cm}^{-1}$ ): 2143 ( $\text{N}_2$ ). Combustion analysis data were reproducibly low in nitrogen, likely due to modest lability of the  $\text{N}_2$  ligand under strong vacuum.

**$(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{Cl})$ .** To a red solution of  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{CH}_3)$  (**1b**, 0.140 g, 0.206 mmol) in THF (10 mL),  $\text{HCl}$  (0.21 mL of 1 M solution in ether, 0.21 mmol) was added at  $-35\text{ }^\circ\text{C}$ . After the reaction mixture was stirred for 1 hr at RT, volatiles were removed under vacuum. The resulting orange solid was dissolved in benzene (5 mL), filtered through Celite and dried. The product  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{Cl})$  (0.140 g, 0.200 mmol, 95%) was obtained as an orange powder after washing with pentane (5 mL x 3) and drying under vacuum. The

identity of the product  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{Cl})$  was confirmed by comparing its  $^1\text{H}$ -NMR data with that of a previously reported sample.<sup>i</sup>  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 7.3, 5.4, 2.6, –2.7.

**$(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)$  (4b).** A dark green solution of sodium naphthalide was prepared by stirring a naphthalene solution (26 mg, 0.202 mmol) in THF (10 mL) over excess sodium metal (26 mg, 1.13 mmol) for 3 hr at RT. The resulting naphthalide solution was filtered away from any remaining sodium and added dropwise at –35 °C to the orange solution of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{Cl})$  (0.140 g, 0.200 mmol) in THF (10 mL), causing a color change to dark red over a period of several minutes. The reaction mixture was stirred overnight at RT, filtered through Celite, and volatiles were removed under vacuum to give a red powder. The residues were extracted into benzene (5 mL), filtered and washed with pentane (5 mL x 2). The resulting product  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)$  (**6b**, 0.100 g, 0.145 mmol, 73%) was isolated as a red powder after drying under vacuum. The identity of the product  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)$  was confirmed by comparing its  $^1\text{H}$ -NMR data with that of an authentic sample.<sup>i</sup>  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 10.0, 7.1, 7.0, 3.8, 2.1, 1.1. IR (KBr pellet;  $\text{cm}^{-1}$ ): 2003 ( $\text{N}_2$ ).

**Oxidation of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)$  (4b).**  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)$  (**4b**, 10 mg, 0.015 mmol) was dissolved in  $\text{C}_6\text{H}_6$  (10 mL) and cooled to –35 °C. After adding  $\text{H}(\text{OEt}_2)_2[\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (15 mg, 0.015 mmol) to the frozen solution the mixture was vigorously stirred for 30 min at RT, resulting in precipitation of a blue solid. The precipitate was collected on a medium porosity glass-frit and washed with benzene (3 x 10 mL) and pentane (3 x 10 mL). The resulting blue-green powder,  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**3**, 22 mg,

0.014 mmol, 93%), was dried under vacuum for a short time. Spectroscopic features in the  $^1\text{H}$ -NMR were identical to that reported above for **3**. IR (KBr pellet;  $\text{cm}^{-1}$ ): 2140 ( $\text{N}_2$ ).  $\text{H}_2(\text{g})$  generated from the reaction was detected by GC analysis.

**$[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(\text{THF})_3]$  (**5**).** A dark green solution of sodium naphthalide was prepared by stirring a naphthalene solution (28 mg, 0.218 mmol) in THF (10 mL) over excess sodium metal (28 mg, 1.22 mmol) for 3 hr at RT. The resulting sodium naphthalide solution was filtered away from any remaining sodium and added dropwise at  $-35\text{ }^\circ\text{C}$  to the red solution of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)$  (**4b**, 0.146 g, 0.211 mmol) in THF (10 mL), causing a color change to dark purple over a period of several minutes. The reaction mixture was stirred overnight at RT, filtered through Celite. Volatiles were removed under vacuum to give a dark purple powder. The solid was collected on a medium porosity glass-frit and washed with pentane (5 mL x 2), benzene/pentane (1/5; 6 mL) and pentane (5 mL x 2). The resulting product  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(\text{THF})_3]$  (**5**, 0.177 g, 0.19 mmol, 90%) was obtained as a dark purple powder after drying under vacuum.  $^1\text{H}$ -NMR (THF- $\text{d}_8$ , ppm): 7.8 (d,  $J = 6.8\text{ Hz}$ , 3H), 7.1 (d,  $J = 7.6\text{ Hz}$ , 3H), 6.9 (t,  $J = 7\text{ Hz}$ , 3H), 6.8 (t,  $J = 7.2\text{ Hz}$ , 3H), 3.6 (THF), 2.5 (bs, 6H), 1.8 (THF), 1.1 (d,  $J = 5.6\text{ Hz}$ , 18H), 0.57 (bs, 18H).  $^{31}\text{P}$ -NMR (THF- $\text{d}_8$ , ppm;  $-70\text{ }^\circ\text{C}$ ): 81.72. Black X-ray quality crystals were grown by diffusion of pentane vapors into a THF solution of **5**; TBP ( $\tau = 1.0$ ). UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 280 {16,000}, 380 {5,200}, 510 {3,600}. IR (KBr pellet;  $\text{cm}^{-1}$ ): 1891 ( $\text{N}_2$ ).

**Alternative synthesis of 5.** A dark green solution of sodium naphthalide was prepared by stirring a naphthalene solution (30 mg, 0.234 mmol) in THF (10 mL) over excess sodium

metal (30 mg, 1.30 mmol) for 3 hr at RT. The resulting sodium naphthalide solution was filtered away from any remaining sodium and added dropwise to the pre-cooled red solution of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{Cl})$  (0.080 g, 0.114 mmol) in THF (10 mL), causing the solution color to change to dark purple over a period of several minutes. The reaction mixture was stirred overnight at RT and then filtered through Celite. Volatiles were removed under vacuum to give a dark purple powder. The solid was collected on a medium porosity glass-frit and washed with pentane (5 mL x 2), benzene/pentane (1/5; 6 mL) and pentane (5 mL x 2). Resulting product **5** (0.090 g, 0.097 mmol, 85%) was obtained as a dark purple powder after drying under vacuum. The identity of the product  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(\text{THF})_3]$  (**5**) was confirmed by its  $^1\text{H}$ -NMR spectrum.

$[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(^{15}\text{N}_2)][\text{Na}(\text{THF})_3]$  (**5**- $^{15}\text{N}_2$ ). A dark green solution of sodium naphthalide was prepared by stirring a naphthalene solution (24 mg, 0.189 mmol) in THF (10 mL) over excess sodium metal (24 mg, 1.04 mmol) for 3 hr at RT. The resulting naphthalide solution was filtered away from sodium and layered on top of the frozen red solution of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{Cl})$  (0.066 g, 0.095 mmol) in THF (10 mL) which was degassed prior to addition by three freeze-pump-thaw cycles. The frozen reaction mixture was taken out of the glovebox, degassed while keeping the  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{Cl})$  solution partially frozen and then exposed to  $^{15}\text{N}_2$  gas (98%+, Cambridge Isotope Laboratories, Inc). The reaction mixture was stirred overnight at RT, filtered through Celite. Volatiles were removed under vacuum to give a dark purple powder. The solid was collected on a glass-frit and washed with pentane (5 mL x 2), benzene/pentane (1/5; 6 mL) and pentane (5 mL x 2). The resulting  $^{15}\text{N}$ -labeled product **5**- $^{15}\text{N}$  (0.075 g, 0.080 mmol, 85%) was obtained as a

dark purple powder after drying under vacuum. Spectroscopic features in the  $^1\text{H}$ -NMR were identical for **5**.  $^{31}\text{P}$ - NMR (THF- $d_8$ , ppm;  $-95\text{ }^\circ\text{C}$ ): 81.36.  $^{15}\text{N}$ - NMR (THF- $d_8$ , ppm, RT): 340.3, 309.7.<sup>ix</sup> IR (KBr pellet;  $\text{cm}^{-1}$ ): 1829.

**$[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$  (**5'**)**. To a dark purple solution of **5** (32 mg, 0.034 mmol) in THF (10 mL) a solution of 12-crown-4 (12 mg, 0.068 mmol) in THF (1 mL) was added. The reaction mixture was stirred for 30 min at RT. The resulting darker solution was filtered through Celite. Volatiles were removed under vacuum to give dark purple powder. The solid was collected, on glass-frit (M) and washed with pentane (3 mL x 3).  **$[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$  (**5'**)**, 35 mg, 0.033 mmol, 97%) was obtained as a dark crystalline solid from recrystallization of **5'** with THF and pentane at room temperature.  $^1\text{H}$ -NMR (THF- $d_8$ , ppm): 7.9 (bs, 3H), 7.1 (d,  $J = 7.0\text{ Hz}$ , 3H), 6.8 (t,  $J = 6.5\text{ Hz}$ , 3H), 6.7 (bs, 3H), 3.6 (32H, 12-c-4), 2.5 (bs, 6H), 1.1 (bs, 18H), 0.63 (bs, 18H).  $^{31}\text{P}$ -NMR (THF- $d_8$ , ppm; measured at  $-70\text{ }^\circ\text{C}$ ): 81.8. Black X-ray quality crystals were grown by diffusion of pentane vapors into a THF solution of **5'**; TBP ( $\tau = 1.0$ ). Anal. Calcd. For  $\text{C}_{52}\text{H}_{86}\text{FeN}_2\text{NaO}_8\text{P}_3\text{Si}$ : C, 58.53; H, 8.12; N, 2.63. Found: C, 58.27; H, 8.09; N, 2.46. UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 280  $\{16,500\}$ , 385  $\{5,800\}$ , 520  $\{3,800\}$ . IR (KBr pellet;  $\text{cm}^{-1}$ ): 1920.

**$[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(^{15}\text{N}_2)][\text{Na}(\text{12-C-4})_2]$  (**5'**- $^{15}\text{N}_2$ )**. To a dark purple solution of  $^{15}\text{N}$ -labeled sample of **7** (15 mg, 0.016 mmol) in THF (10 mL) a solution of 12-crown-4 (6 mg, 0.034 mmol) in THF (1 mL) was added. The reaction mixture was stirred for 30 min at RT. The resulting solution was filtered through Celite and volatiles were removed under



vacuum to give a dark purple powder. The solid was collected on glass-frit and washed with pentane (3 mL x 3).  $[(\text{SiP}^{\text{Pr}}_3)\text{Fe}(^{15}\text{N}_2)][\text{Na}(\text{12-C-4})_2]$  (**5'**- $^{15}\text{N}_2$ , 16 mg, 0.015 mmol, 94%) was obtained as a dark solid after drying under vacuum. Spectroscopic features in the  $^1\text{H}$ -NMR were identical to **7'**.  $^{31}\text{P}$ -NMR (THF- $\text{d}_8$ , ppm;  $-70^\circ\text{C}$ ): 81.8.  $^{15}\text{N}$ -NMR (THF- $\text{d}_8$ , ppm, RT): 350.6, 313.1. IR (KBr pellet;  $\text{cm}^{-1}$ ): 1855 ( $^{15}\text{N}_2$ ).

**$\text{N}_2\text{H}_5\bullet\text{CF}_3\text{SO}_3$** . Triflic acid (3.0 g, 20.0 mmol) was added to a cold solution of anhydrous  $\text{N}_2\text{H}_4$  (1.0 g, 31.2 mmol) dissolved in THF (100 mL) at  $0^\circ\text{C}$ . After warming to room temperature the reaction mixture was stirred for 30 min, and then all volatiles were removed by vacuum. The colorless product (2.97 g, 16.3 mmol, 82%) was obtained as an oil by washing with diethyl ether (3 x 20 mL) and drying under vacuum.  $^1\text{H}$ -NMR (THF- $\text{d}_8$ , ppm): 6.0 (bs, 2H), 5.9 (bs, 3H).  $^1\text{H}$ -NMR ( $\text{CD}_3\text{CN}$ , ppm): 5.49 (bs, 3H), 5.49 (bs, 2H).  $^{19}\text{F}$ -NMR ( $\text{CD}_3\text{CN}$ , ppm):  $-77.1$ . IR (KBr pellet;  $\text{cm}^{-1}$ ): 3309, 2984, 2773, 2726.

**$[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6a**•OTf)**.  **$\text{N}_2\text{H}_5\bullet\text{CF}_3\text{SO}_3$**  (0.318 g, 1.75 mmol) dissolved in THF (5 mL) was slowly added to a THF solution (15 mL) of  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{CH}_3)$  (**1a**, 1.1 g, 1.25 mmol) with vigorous stirring at room temperature. The resulting dark red solution was stirred for 1 hr, filtered through Celite and concentrated to 10 mL. A red wine crystalline product was obtained from a THF solution layered with pentane at RT. The resulting product,  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6a**•OTf, 1.26 g, 1.2 mmol, 96%), was collected on a medium porosity sintered glass frit, washed with additional pentane, and dried by vacuum.  $^1\text{H}$ -NMR (THF- $\text{d}_8$ , ppm): 12.9, 5.5, 4.9, 2.5, 2.3, 2.2,  $-3.4$ ,  $-4.4$ .

$^{19}\text{F}$ -NMR (THF- $d_8$ , ppm):  $-76.1$ .  $\mu_{\text{eff}}$ (THF- $d_8$ ,  $20^\circ\text{C}$ ):  $2.79 \mu_{\text{B}}$ . Red X-ray quality crystals were grown by diffusion of pentane vapors into a THF solution of **6a•OTf**; TBP ( $\tau = \sim 0.9$ ). UV-Vis (THF, nm  $\{\text{cm}^{-1} \text{M}^{-1}\}$ ):  $412 \{4,200\}$ ,  $494 \{2,700\}$ . IR (KBr pellet;  $\text{cm}^{-1}$ ):  $3359, 3311, 3277, 3223, 3161$ .

$[(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**6a•B(ArF)<sub>4</sub>**).  $\text{H}(\text{OEt}_2)_2[\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  ( $0.229 \text{ g}, 0.226 \text{ mmol}$ ) was added to tetrahydrofuran solution ( $20 \text{ mL}$ ) of  $(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{CH}_3)$  (**1a**,  $0.200 \text{ g}, 0.226 \text{ mmol}$ ) with vigorous stirring at  $-35^\circ\text{C}$ . The resulting dark red mixture was stirred for  $2 \text{ hr}$  at room temperature. Hydrazine ( $0.060 \text{ g}, 1.87 \text{ mmol}$ ) dissolved in THF ( $5 \text{ mL}$ ) was slowly added to the dark red solution at  $-35^\circ\text{C}$ . After filtration through Celite the resulting dark red solution was concentrated to  $5 \text{ mL}$ .  $[(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**6a•B(ArF)<sub>4</sub>**,  $0.35 \text{ g}, 0.199 \text{ mmol}$ ,  $88\%$ ) was obtained from layering pentane over a concentrated solution, resulting in precipitation of a red powder that was collected on a medium porosity sintered glass frit. The product was washed with additional pentane and dried under vacuum.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm):  $12.8, 8.4, 7.71, 5.1, 2.5, -3.9, -4.9$ .  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm):  $-61.6$  ppm.  $\mu_{\text{eff}}$ (THF- $d_8$ ,  $20^\circ\text{C}$ ):  $3.00 \mu_{\text{B}}$ . Red X-ray quality crystals were grown by diffusion of pentane vapors into a THF solution of **6a•B(ArF)<sub>4</sub>**; TBP ( $\tau = \sim 0.9$ ). Anal. Calcd. For  $\text{C}_{86}\text{H}_{58}\text{BF}_{24}\text{FeN}_2\text{P}_3\text{Si}$ : C,  $58.59$ ; H,  $3.32$ ; N,  $1.59$ . Found: C,  $57.96$ ; H,  $4.02$ ; N,  $1.24$ . UV-Vis (THF, nm  $\{\text{cm}^{-1} \text{M}^{-1}\}$ ):  $409 \{3,900\}$ ,  $492 \{2,300\}$ ,  $1100 \{200\}$ . IR (KBr pellet;  $\text{cm}^{-1}$ ):  $3400, 3357, 3325, 3273, 3252$ .

**$[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6b•OTf**).**  $\text{N}_2\text{H}_5\text{CF}_3\text{SO}_3$  (0.025 g, 0.137 mmol) dissolved in THF (5 mL) was slowly added to an orange THF solution (5 mL) of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{CH}_3)$  (**1b**, 0.094 g, 0.139 mmol) with vigorous stirring at room temperature. The resulting red solution was stirred for 1 hr, filtered through Celite and concentrated to 3 mL. A red crystalline product was obtained from THF solution layered with pentane at room temperature. The resulting product,  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6b•OTf**, 0.080 g, 0.095 mmol, 69%), was collected after the supernatant was decanted. The solid was washed with additional pentane and dried under vacuum.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6/\text{THF-d}_8$ , ppm): 6.0,  $-0.8$ ,  $-3.7$ ,  $-4.8$ .  $^{19}\text{F-NMR}$  ( $\text{C}_6\text{D}_6/\text{THF-d}_8$ , ppm):  $-74.8$  ppm.  $\mu_{\text{eff}}$  (THF- $\text{d}_8$ , 20 °C):  $3.0 \mu_{\text{B}}$ . Orange X-ray quality crystals were grown by diffusion of pentane vapors into a THF solution of **6b•OTf**; TBP ( $\tau = 0.96$ ). UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 406 {3,100}, 492 {1,560}, 900 {20}. IR (KBr pellet;  $\text{cm}^{-1}$ ): 3390, 3299, 3274, 3230, 3155.

**$[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  (**6b•B(ArF)<sub>4</sub>**).**  $\text{N}_2\text{H}_4$  (0.010 g, 0.312 mmol) dissolved in THF (5 mL) was added to an orange THF solution (10 mL) of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{CH}_3)$  (**1b**, 0.100 g, 0.147 mmol) with vigorous stirring at room temperature. After  $\text{H}(\text{OEt}_2)_2[\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  (0.149 g, 0.147 mmol) was added at  $-35$  °C the resulting red solution was stirred for 1 hr. The solution was filtered through Celite and concentrated to 3 mL. An orange crystalline product was obtained by layering the THF solution with pentane at  $-35$  °C overnight. After the supernatant was decanted the resulting solid was washed with benzene/pentane (3/10) and pentane ( $3 \times 5$  mL). The resulting product,  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  (**6b•B(ArF)<sub>4</sub>**, 0.163 g, 0.105 mmol, 71%), was collected after drying under vacuum.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6/\text{THF-d}_8$ , ppm):

8.20, 7.64, 5.84, 0.4, -0.8, -4.39.  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6/\text{THF-d}_8$ , ppm): -60.7 ppm.  $\mu_{\text{eff}}$  (THF- $\text{d}_8$ , 20 °C): 3.3  $\mu_{\text{B}}$ . Anal. Calcd. For  $\text{C}_{68}\text{H}_{70}\text{BF}_{24}\text{FeN}_2\text{P}_3\text{Si}$ : C, 52.39; H, 4.53; N, 1.80. Found: C, 52.70; H, 4.42; N, 1.79. UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 406 {2,800}, 500 {1,250}, 530 {sh}, 900 {20}. IR (KBr pellet;  $\text{cm}^{-1}$ ): 3407, 3324, 3260.

**Reduction of 6a and 6b.** In a 2-neck 25-mL round-bottomed flask,  $[(\text{SiP}^{\text{R}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6a** or **6b**, 25-30 mg) and 1 equiv of  $\text{Cp}^*_2\text{Cr}$  were dissolved in THF (3 mL) and sealed with septa under a nitrogen atmosphere. After the reaction mixture was stirred for 30 min at RT, the reaction volatiles were vacuum-transferred onto a frozen HCl solution (5 mL, 1.0 M in  $\text{Et}_2\text{O}$ ). The mixture was allowed to warm and stirred for 30 min at RT and then concentrated to white solids by rotary evaporation.  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ) analysis was performed with mesitylene added as an internal integration standard.  $[\text{N}_2\text{H}_5]\text{Cl}^{\text{i}}$  and  $[\text{NH}_4]\text{Cl}^{\text{x}}$  were detected with modest yields 10-20 and 50-60%, respectively based on  $^1\text{H}$ -NMR integration. In an NMR tube equipped with a J-young valve, 1 equiv  $\text{Cp}^*_2\text{Cr}$  was added to a  $\text{C}_6\text{D}_6/\text{THF-d}_8$  (5/1) solution of  $[(\text{SiP}^{\text{R}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  at -78 °C. The reaction was monitored by  $^1\text{H}$ -NMR at room temperature. The identity of the product  $(\text{SiP}^{\text{R}}_3)\text{Fe}(\text{N}_2)$  was confirmed by  $^1\text{H}$ -NMR and IR data by comparing with authentic samples.<sup>i</sup> Hydrazine ( $\text{N}_2\text{H}_4$ ) and  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  liberated during the reaction were detected by  $^1\text{H}$ -NMR spectroscopy.

$[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  (**7a**).  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{THF})][\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  (**2a**) (0.153 g, 0.085 mmol) was dissolved in tetrahydrofuran (20 mL) in a 50 mL Schlenk tube. The reaction tube was evacuated and then charged with ammonia (1 atm). The

reaction mixture darkened upon stirring at RT for 30 min. All volatiles were removed under vacuum, and the resulting red powder was washed with pentane and dried under vacuum.  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7a**, 0.135 g, 0.077 mmol, 90%) was obtained as a red powder.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , ppm): 13.2, 8.7, 7.8, 5.1, 4.8, 1.7,  $-3.7$ ,  $-5.0$ .  $^{19}\text{F-NMR}$  ( $\text{C}_6\text{D}_6$ , ppm):  $-64.0$  ppm.  $\mu_{\text{eff}}$  ( $\text{THF-d}_8$ , 20 °C):  $3.33 \mu_{\text{B}}$ . Red X-ray quality crystals were grown by diffusion of pentane vapors into a THF solution of **7a**; TBP ( $\tau = 0.87$ ). Anal. Calcd. For  $\text{C}_{86}\text{H}_{57}\text{BF}_{24}\text{FeNP}_3\text{Si}$ : C, 59.09; H, 3.29; N, 0.80. Found: C, 57.62; H, 3.38; N, 0.96. UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 408 {2,600}, 490 {1,590}, 530 {sh}, 1,100 {150}. IR (KBr pellet;  $\text{cm}^{-1}$ ): 3365, 3348, 3278, 3202.

$[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7b**).  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**3**) (0.100 g, 0.064 mmol) was dissolved in tetrahydrofuran (20 mL) in a 50 mL Schlenk tube. The reaction tube was evacuated and then charged with ammonia (1 atm). The reaction mixture darkened while stirring at RT for 30 min. All volatiles were removed under vacuum, and the resulting red powder was washed with additional benzene and then pentane, and dried under vacuum.  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7b**, 0.095 g, 0.062 mmol, 96%) was obtained as a red powder.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6/\text{THF-d}_8$ , ppm): 8.3, 7.7, 6.3, 5.4,  $\sim 1$ ,  $-3.9$ .  $^{19}\text{F-NMR}$  ( $\text{C}_6\text{D}_6/\text{THF-d}_8$ , ppm):  $-64.6$  ppm.  $\mu_{\text{eff}}$  ( $\text{THF-d}_8$ , 20 °C):  $3.27 \mu_{\text{B}}$ . Dark red X-ray quality crystals were grown by diffusion of pentane vapors into a benzene solution of **7b**; TBP ( $\tau = 1.0$ ). Anal. Calcd. For  $\text{C}_{86}\text{H}_{69}\text{BF}_{24}\text{FeNP}_3\text{Si}\cdot\text{NH}_3$ : C, 52.32; H, 4.65; N, 1.79. Found: C, 51.97; H, 4.56; N, 1.77. UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 403 {2,340}, 486 {1,060}, 520 {sh}, 920 {55}. IR (KBr pellet;  $\text{cm}^{-1}$ ): 3377, 3293, 3199.

**Reduction of  $[(\text{SiP}^{\text{R}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7a** and **7b**).** In a 2-neck 25-mL round-bottomed flask,  $[(\text{SiP}^{\text{R}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7a** or **7b**, 15-20 mg) and 1 equiv of  $\text{Cp}^*\text{Cr}$  were dissolved in THF (3 mL) and sealed with septa under a nitrogen atmosphere. After the reaction mixture was stirred for 1 hr at RT, the reaction volatiles were vacuum-transferred onto a frozen HCl solution (5 mL, 1.0 M in  $\text{Et}_2\text{O}$ ). The mixture was allowed to warm and stirred for 30 min at RT and then concentrated to white solids by rotary evaporation.  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ) analysis was performed with mesitylene added as an internal integration standard.  $[\text{NH}_4]\text{Cl}$  was detected in 90-94% yields based on  $^1\text{H}$ -NMR integration.<sup>x</sup> In a separate experiment, 1 equiv of  $\text{Cp}^*\text{Cr}$  was added to a  $\text{C}_6\text{D}_6/\text{THF-d}_8$  (5/1) solution of  $[(\text{SiP}^{\text{R}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  in an NMR tube with a J-Young valve at  $-78^\circ\text{C}$ . The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy at room temperature. The identity of the product  $(\text{SiP}^{\text{R}}_3)\text{Fe}(\text{N}_2)$  was confirmed by  $^1\text{H}$ -NMR and IR data by comparison with data for authentic samples.<sup>i</sup>

**$\{\text{Si}(o\text{-C}_6\text{H}_4\text{PPh}_2)_2(o\text{-C}_6\text{H}_4\text{P(=NH)Ph}_2)]\text{Fe}(\text{NH}_3)\}\{\text{CF}_3\text{SO}_3\}$  (**8**).** A red THF (1 mL) solution of  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6b**, 0.051 g, 0.048 mmol) was slowly added to the toluene (9 mL) solution of  $N^1, N^1, N^8, N^8$ -tetramethylnaphthalene-1,8-diamine (proton sponge, 0.040 g, 0.187 mmol) with vigorous stirring. The reaction mixture was stirred overnight at room temperature. The resulting red solution was filtered through Celite and volatiles were removed under vacuum. Resulting powder was washed with pentane and dried under vacuum. The crude mixture contains **8** with **6b** and  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{NH}_3)][\text{CF}_3\text{SO}_3]$  as analyzed by  $^1\text{H}$ -NMR.  $\{\text{Si}(o\text{-C}_6\text{H}_4\text{PPh}_2)_2(o\text{-C}_6\text{H}_4\text{P(=NH)Ph}_2)]\text{Fe}(\text{NH}_3)\}\{\text{CF}_3\text{SO}_3\}$  (**8**).

$\text{C}_6\text{H}_4\text{P}(=\text{NH})\text{Ph}_2)]\text{Fe}(\text{NH}_3)\{\text{CF}_3\text{SO}_3\}$  (**8**) was identified by XRD data using dark red crystals obtained from a THF solution layered with pentane at room temperature; TBP ( $\tau = 0.85$ ). However, pure material free of **6b** and  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{NH}_3)][\text{CF}_3\text{SO}_3]$  could not be obtained.  $^1\text{H}$ -NMR peaks for representing **8** ( $\text{C}_6\text{D}_6$ , ppm): 12.4, 5.4, 5.0,  $-3.6$ ,  $-4.3$ .

**$\text{N}_2\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3$** . Anhydrous hydrazine (0.027 g, 0.84 mmol) dissolved in THF (5 mL) was slowly added to a THF solution (5 mL) of tris(pentafluorophenyl)borane (0.437 g, 0.84 mmol). The reaction mixture was stirred for 1 hr at RT and filtered through Celite. After the colorless solution was concentrated under vacuum, pentane (10 mL) was slowly added to the resulting colorless oil ( $\sim 1$  mL). Standing at RT for 1 hr resulted in the formation of small crystals. The solution was allowed to stand at  $-35$  °C for an additional hour. The supernatant was decanted and the resulting crystalline product  $\text{N}_2\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3$  (0.235 g, 0.432 mmol, 51 %) was dried under vacuum.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 4.7 (bs, 2H), 2.1 (t,  $J = 5.1$  Hz, 2H).  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm):  $-132.9$  (d,  $J = 23.7$  Hz),  $-153.2$  (t,  $J = 21.1$  Hz),  $-161.7$  (m).  $^{11}\text{B}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm):  $-7.2$ . Anal. Calcd. For  $\text{C}_{18}\text{H}_4\text{BF}_{15}\text{N}_2$ : C, 39.74; H, 0.74; N, 5.15. Found: C, 39.91; H, 1.12; N, 5.06. IR (KBr pellet;  $\text{cm}^{-1}$ ): 3387, 3322, 3298, 3140.

**$(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)$  (**9a**)**.  $\text{N}_2\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3$  (61 mg, 0.112 mmol) dissolved in THF (5 mL) was slowly added to the pre-cooled ( $-35$  °C) THF (5 mL) solution of  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{CH}_3)$  (**1a**, 100 mg, 0.113 mmol). The reaction mixture was stirred for 3 hr at RT. The resulting red solution was filtered through Celite and all volatiles were removed under vacuum. The resulting red powder was dissolved in benzene (5 mL) and filtered

through Celite. Pentane (15 mL) was slowly layered and the solution was allowed to stand at  $-35\text{ }^{\circ}\text{C}$  overnight. The supernatant was decanted and the red product,  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)$  (**9a**, 0.126 g, 0.089 mmol, 79.5%), was dried under vacuum.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 12.5, 5.3, 4.9, 2.1,  $-3.9$ ,  $-4.2$ ,  $-5.3$ .  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm):  $-122$ ,  $-157$ ,  $-162$ .  $\mu_{\text{eff}}$  ( $\text{C}_6\text{D}_6$ ,  $20\text{ }^{\circ}\text{C}$ ):  $2.9\text{ }\mu_{\text{B}}$ . Red X-ray quality crystals were grown by diffusion of pentane vapors into a THF solution of **9a**; TBP ( $\tau = 0.94$ ). Anal. Calcd. For  $\text{C}_{77}\text{H}_{57}\text{BF}_{15}\text{FeN}_2\text{P}_3\text{Si}$ : C, 62.36; H, 3.87; N, 1.89. Found: C, 62.35; H, 3.87; N, 1.72. UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 416  $\{3,800\}$ , 495  $\{2,100\}$ , 1,100  $\{200\}$ . IR (KBr pellet;  $\text{cm}^{-1}$ ): 3395, 3372, 3326, 3273, 3183.

**$(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)$  (**9b**)**.  $\text{N}_2\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3$  (78.6 mg, 0.144 mmol) dissolved in THF (5 mL) was slowly added to the pre-cooled ( $-35\text{ }^{\circ}\text{C}$ ) THF (5 mL) solution of  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{CH}_3)$  (**2a**, 98 mg, 0.144 mmol). The reaction mixture was stirred for 3 hr at RT. The resulting orange solution was filtered through Celite and all volatiles were removed under vacuum. The resulting orange powder was dissolved in benzene (0.5 mL) with pentane (1 mL) and filtered through Celite. Pentane was slowly added and the solution was allowed to stand at  $-35\text{ }^{\circ}\text{C}$  overnight. The supernatant was decanted and the orange product  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)$  was dried under vacuum and obtained (**9b**, 168 mg, 0.139 mmol, 96%).  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 25.7, 6.3, 5.5,  $\sim 0$ ,  $-1.5$ ,  $-4.4$ .  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm):  $-125$ ,  $-157$ ,  $-162$ .  $\mu_{\text{eff}}$  ( $\text{C}_6\text{D}_6$ ,  $20\text{ }^{\circ}\text{C}$ ):  $2.83\text{ }\mu_{\text{B}}$ . Orange X-ray quality crystals were obtained from the concentrated pentane solution of **9b** at  $-35\text{ }^{\circ}\text{C}$ , TBP ( $\tau = 0.85$ ). Anal. Calcd. For  $\text{C}_{59}\text{H}_{69}\text{BF}_{15}\text{FeN}_2\text{P}_3\text{Si}$ : C, 55.41; H, 5.44; N, 2.19. Found: C,



54.37; H, 5.31; N, 1.90. UV-Vis (THF, nm { $\text{cm}^{-1}\text{M}^{-1}$ }): 413 {2,400}, 493 {1,200}, 530 {sh}, 914 {90}. IR (KBr pellet;  $\text{cm}^{-1}$ ): 3433, 3291, 3245.

**$\text{N}_2\text{H}_4\text{C}_6\text{H}_5\bullet\text{CF}_3\text{SO}_3$ .** Triflic acid (3.75 g, 24.5 mmol) was added to a cold solution of  $\text{N}_2\text{H}_3\text{C}_6\text{H}_5$  (2.73 g, 24.5 mmol) dissolved in THF (100 mL) at  $-15^\circ\text{C}$ . After warming to room temperature the reaction mixture was stirred for 30 min, and all volatiles were removed under vacuum. A white powder (6.0 g, 23.2 mmol, 95%) was collected, washed with pentane (3 x 30 mL) and dried under vacuum.  $^1\text{H}$ -NMR (THF- $d_8$ , ppm): 9.6 (bs, 3H), 7.7 (bs, 1H), 7.3 (m, 2H), 7.0 (m, 3H).  $^1\text{H}$ -NMR ( $\text{CD}_3\text{CN}$ , ppm): 8.0 (bs, 4H), 7.4 (m, 2H), 7.1 (m, 1H), 7.0 (m, 2H).  $^{19}\text{F}$ -NMR ( $\text{CD}_3\text{CN}$ , ppm):  $-77.1$ . IR (KBr pellet;  $\text{cm}^{-1}$ ): 3309, 2984.

**$(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{C}_6\text{H}_5)$  (**10**).**  $\text{N}_2\text{H}_4\text{C}_6\text{H}_5\bullet\text{CF}_3\text{SO}_3$  (0.059 g, 0.228 mmol) was added to an orange THF solution (50 mL) of  $(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{CH}_3)$  (**1b**, 0.200 g, 0.227 mmol) at  $-35^\circ\text{C}$ , and slowly warmed to room temperature. The solution was vigorously stirred for 30 min. After addition of Phenylhydrazine (0.05 g, 0.46 mmol) the resulting dark red solution was stirred for 3 days at  $70^\circ\text{C}$ . The reaction mixture was brought into a dry-box and all volatiles were removed under vacuum. The dark brown crude material was dissolved in benzene (30 mL) and stirred for 30 min at room temperature. Pentane was added slowly, resulting in a cloudy solution that was filtered through Celite and concentrated under vacuum.  $(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{C}_6\text{H}_5)$  (**10**, 0.166 g, 0.171 mmol, 75%) was obtained as a dark brown solid after washing with additional portions of pentane (3 x 3 mL) and drying under vacuum. The pentane supernatant was concentrated and dried under vacuum. The

resulting brown oil (44 mg) was analyzed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy and GC/MS. The major organic product (>50 %) was identified as aniline.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 6.0, -0.8, -3.7, -4.8.  $\mu_{\text{eff}}$  (THF- $d_8$ , 20  $^\circ\text{C}$ ): 3.0  $\mu_{\text{B}}$ . Dark brown X-ray quality crystals were grown by diffusion of pentane vapors into a benzene solution of **10**; TBP ( $\tau$  = 0.89). Anal. Calcd. For  $\text{C}_{60}\text{H}_{47}\text{FeN}_2\text{P}_3\text{Si}$ : C, 74.25; H, 5.36; N, 3.27. Found: C, 74.07; H, 4.87; N, 2.88. UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 420 {sh}, 478 {3,800}, 570 {sh}, 1100 {100}. IR (KBr pellet;  $\text{cm}^{-1}$ ): 1623.

$[(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{C}_6\text{H}_5)][\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  (**11**).  $[(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{THF})][\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  (**2a**) (0.140 g, 0.078 mmol) was dissolved in tetrahydrofuran (15 mL). Phenylhydrazine (0.040 g, 0.37 mmol) dissolved in THF (5 mL) was added to the solution with vigorous stirring at -78  $^\circ\text{C}$ . The red mixture<sup>xi</sup> was stirred for 2 days at room temperature. After filtration through Celite, the dark red solution was concentrated to 5 mL.  $[(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{C}_6\text{H}_5)][\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$  (**11**, 0.061 g, 0.033 mmol, 43%) was obtained as black crystals by layering pentane over a concentrated THF solution and allowing to stand for a 3 days at -35  $^\circ\text{C}$ . The product was collected on a sintered glass frit, washed with additional pentane and dried under vacuum.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 10.2, 8.7, 8.5, 7.7, 7.1, 4.3, 3.7, -0.5.  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): -60.3.  $\mu_{\text{eff}}$  ( $\text{C}_6\text{D}_6$ , 20  $^\circ\text{C}$ ): 1.85  $\mu_{\text{B}}$ . Black X-ray quality crystals were grown by diffusion of pentane vapors into a benzene solution of **11**; TBP ( $\tau$  = 0.90). Anal. Calcd. For  $\text{C}_{92}\text{H}_{59}\text{BF}_{24}\text{FeN}_2\text{P}_3\text{Si}$ : C, 60.18; H, 3.24; N, 1.53. Found: C, 60.47; H, 3.56; N, 1.85. UV-Vis (THF, nm  $\{\text{cm}^{-1}\text{M}^{-1}\}$ ): 540 {600}, 1040 {150}. IR (KBr pellet;  $\text{cm}^{-1}$ ): 1690.

**(SiP<sup>iPr</sup><sub>3</sub>)Fe(N<sub>2</sub>SiMe<sub>3</sub>) (12).** To the frozen dark solution of [(SiP<sup>iPr</sup><sub>3</sub>)Fe(N<sub>2</sub>)] [Na(THF)<sub>3</sub>] (**5**, 53 mg, 0.056 mmol) in THF (10 mL), trimethylsilyl chloride (7.1  $\mu$ L, 0.056 mmol) was added. The reaction mixture was slowly warmed to room temperature and vigorously stirred for overnight. All volatiles were removed by vacuum and the resulting dark oil was dissolved in pentane, filtered through Celite and volatiles were removed by vacuum. Resulting product (SiP<sup>iPr</sup><sub>3</sub>)Fe(N<sub>2</sub>SiMe<sub>3</sub>) (**12**, 41 mg, 0.054 mmol, <96%)<sup>xii</sup> was obtained as a reddish black powder after drying under vacuum. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 8.02 (d, *J* = 6.3 Hz, 3H), 7.30 (d, *J* = 7.2 Hz, 3H), 7.21 (t, *J* = 7.2 Hz, 3H), 7.06 (t, *J* = 7.2 Hz, 3H), 2.57 (bs, 6H), 1.14 (m, 18H), 0.71 (bs, 18H), 0.33 (s, 9H). <sup>31</sup>P-NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 95.6 (s). <sup>29</sup>Si-NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 84.3 (q, <sup>2</sup>*J*<sub>SiP</sub> = 38 Hz), -15.6 (s); TMS-Cl: 29.7 ppm. Dark red X-ray quality crystals were grown from the concentrated THF/pentane solution of **12** at -35 °C; TBP ( $\tau$  = 0.93). UV-Vis (THF, nm {cm<sup>-1</sup> M<sup>-1</sup>}): 270 {16,400}, 310 {sh, 11,000}, 395 {4,900}. IR (KBr pellet; cm<sup>-1</sup>): 1748 (N<sub>2</sub>).

**Alternative synthesis of 12.** A 0.5 weight % Na/Hg amalgam (2.0 mg, 0.087 mmol of sodium dissolved in 400 mg of mercury) was stirred in THF (3 mL). Trimethylsilyl chloride (15.4 mg, 0.142 mmol) was added directly to the stirring solution of amalgam. A solution of **4b** (50 mg, 0.072 mmol) in THF (5 mL) was added to the mixture at room temperature. The combined solution was stirred for 5 hr, after which time the solution was filtered to remove mercury and precipitates. All volatiles were removed and dried under vacuum. The product **12** (51 mg, 0.067 mmol, 93%) was obtained as a reddish black powder. The identity of product was confirmed by <sup>1</sup>H-NMR and IR. Anal. Calcd.

For  $C_{39}H_{63}FeN_2P_3Si_2 \cdot 1/2 C_3H_9ClSi$ : C, 59.38; H, 8.31; N, 3.42. Found: C, 58.90; H, 8.14; N, 3.47.

**$(SiP^{iPr}_3)Fe(^{15}N_2SiMe_3)$  (**12- $^{15}N_2$** ).** To the frozen dark solution of  $\{Na(THF)_3\} \{(SiP^{iPr}_3)Fe(^{15}N_2)\}$  (**5- $^{15}N_2$** , 50 mg, 0.054 mmol) in THF (10 mL), trimethylsilyl chloride (6.8  $\mu$ L, 0.054 mmol) was added. The reaction mixture was slowly warmed to room temperature and vigorously stirred for overnight. All volatiles were removed by vacuum and the resulting dark oil was dissolved in pentane. The dark solution was filtered through Celite and volatiles were removed by vacuum. Resulting product  $(SiP^{iPr}_3)Fe(^{15}N_2SiMe_3)$  (**12- $^{15}N_2$** , 40 mg, 0.052 mmol, 96%) was obtained as a dark powder after drying under vacuum. Spectroscopic features in the  $^1H$ -NMR were identical for **12- $^{15}N_2$** .  $^{31}P$ -NMR (Tol- $d_8$ , ppm; measured at  $-90^\circ C$ ): 90.1 (s).  $^{29}Si$ -NMR (Tol- $d_8$ , ppm; measured at room temperature for 5 hrs): 83.9 (q,  $^2J_{SiP} = 38.7$  Hz),  $-15.9$  (dd,  $^1J_{SiN} = 10$  Hz,  $^2J_{SiN} = 2.2$  Hz).  $^{15}N$ -NMR (Tol- $d_8$ , ppm, measured at RT for 1 hr): 418.8 (d,  $^1J_{NN} = 13.2$  Hz), 271.0 (dd,  $^1J_{NN} = 13.3$  Hz,  $^1J_{NSi} = 3.4$  Hz). IR (KBr pellet;  $cm^{-1}$ ): 1694 ( $^{15}N_2$ ).

**$(SiP^{iPr}_3)Fe(N_2Si^iPr_3)$ .** To the frozen dark solution of  $[(SiP^{iPr}_3)Fe(N_2)][Na(THF)_3]$  (**5**, 28 mg, 0.030 mmol) in THF (10 mL), triisopropylsilyl triflate (8.2  $\mu$ L, 0.030 mmol) was added. The reaction mixture was slowly warmed to room temperature and vigorously stirred for overnight. All volatiles were removed by vacuum and the resulting dark oil was dissolved in pentane, filtered through Celite and volatiles were removed by vacuum. Resulting product  $(SiP^{iPr}_3)Fe(N_2Si^iPr_3)$  (23 mg, 0.027 mmol, <90%)<sup>xii</sup> was obtained as a

reddish black powder after dried by vacuum.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 8.00 (d,  $J = 6.6$  Hz, 3H), 7.32 (d,  $J = 7.5$  Hz, 3H), 7.21 (t,  $J = 7.2$  Hz, 3H), 7.06 (t,  $J = 7.8$  Hz, 3H), 2.63 (bs, 6H), 1.38 (m, 3H), 1.27 (s, 9H), 1.25 (s, 9H), 1.17 (m, 18H), 0.76 (bs, 18H).  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 93.8 (s). IR (KBr pellet;  $\text{cm}^{-1}$ ): 1730 ( $\text{N}_2$ ). No combustion analysis data has been obtained for this compound.

**( $\text{SiP}^{i\text{Pr}}_3$ )Fe( $\text{N}_2\text{SiPh}_3$ ).** A 0.5 weight % Na/Hg amalgam (3.0 mg, 0.087 mmol of sodium dissolved in 400 mg of mercury) was stirred in THF (3 mL) at room temperature. Triphenylsilyl chloride (30 mg, 0.098 mmol) was added directly to the stirring solution of amalgam. A solution of **4b** (50 mg, 0.072 mmol) in THF (5 mL) was added to the mixture at room temperature. The combined solution was stirred for overnight, after which time the dark green solution was filtered to remove mercury and precipitates. All volatiles were removed under vacuum, and the resulting powder was washed with pentane and dried under vacuum. Analytically pure ( $\text{SiP}^{i\text{Pr}}_3$ )Fe( $\text{N}_2\text{SiPh}_3$ ) (53 mg, 0.056 mmol, 78%) was obtained as a dark brown solid by recrystallization from benzene and pentane at  $-35^\circ\text{C}$ .  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 7.9 (m, 9H), 7.2 (m, 15H), 7.02 (t,  $J = 7.2$  Hz, 3H), 2.58 (bs, 6H), 1.13 (m, 18H), 0.62 (bs, 18H).  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 95.1 (s).  $^{29}\text{Si}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm): 83.9 (q,  $^2J_{\text{SiP}} = 40$  Hz),  $-41.7$  (s);  $\text{Ph}_3\text{Si-Cl}$ : 2.0 ppm. Anal. Calcd. For  $\text{C}_{54}\text{H}_{69}\text{FeN}_2\text{P}_3\text{Si}_2$ : C, 68.19; H, 7.31; N, 2.95. Found: C, 67.84; H, 7.23; N, 2.67. UV-Vis (THF, nm { $\text{cm}^{-1}\text{M}^{-1}$ }): 262 {32,000}, 283 {31,000}, 395 {6,700}, 596 {2,300}. IR (KBr pellet;  $\text{cm}^{-1}$ ): 1744 ( $\text{N}_2$ ).

**(SiP<sup>iPr</sup><sub>3</sub>)Fe(<sup>15</sup>N<sub>2</sub>SiPh<sub>3</sub>).** To the frozen dark solution of [(SiP<sup>iPr</sup><sub>3</sub>)Fe(<sup>15</sup>N<sub>2</sub>)] [Na(12-C-4)<sub>2</sub>] (**5'**-<sup>15</sup>N<sub>2</sub>, 65 mg, 0.061 mmol) in THF (10 mL), triphenylsilyl chloride (20 mg, 0.065 mmol) was added. The reaction mixture was slowly warmed to room temperature and vigorously stirred for 4 hrs. All volatiles were removed by vacuum and the resulting dark oil was dissolved in benzene. The dark solution was filtered through Celite and volatiles were removed by vacuum. Resulting product (SiP<sup>iPr</sup><sub>3</sub>)Fe(<sup>15</sup>N<sub>2</sub>SiPh<sub>3</sub>) (43 mg, 0.045 mmol, 74%) was obtained as a dark green powder after washing with pentane (5 mL) and drying under vacuum. Spectroscopic features in the <sup>1</sup>H-NMR were identical for (SiP<sup>iPr</sup><sub>3</sub>)Fe(N<sub>2</sub>SiPh<sub>3</sub>). <sup>31</sup>P-NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 95.1 (s). <sup>29</sup>Si-NMR (C<sub>6</sub>D<sub>6</sub>, ppm; measured at room temperature for 4.6 hrs): 83.7 (qm, <sup>2</sup>J<sub>SiP</sub> = 39.7 Hz, <sup>2</sup>J<sub>SiN</sub> = 3.3 Hz), -41.9 (dd, <sup>1</sup>J<sub>SiN</sub> = 16 Hz, <sup>2</sup>J<sub>SiN</sub> = 3.1 Hz). <sup>15</sup>N- NMR (C<sub>6</sub>D<sub>6</sub>, ppm, measured at RT for 2 hrs): 423.0 (d, <sup>1</sup>J<sub>NN</sub> = 13.4 Hz), 265.7 (d, <sup>1</sup>J<sub>NN</sub> = 13.9 Hz). IR (KBr pellet; cm<sup>-1</sup>): 1687 (<sup>15</sup>N<sub>2</sub>).

Figure S1.  $^1\text{H}$ -NMR spectrum of  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{CH}_3)$  (**1a**) in  $\text{C}_6\text{D}_6$ .

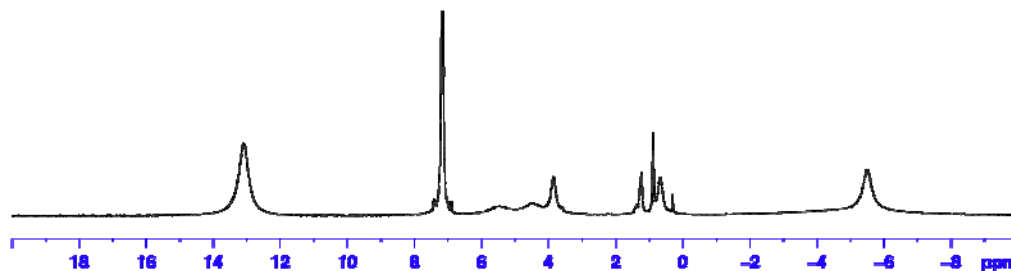


Figure S2.  $^1\text{H}$ -NMR spectrum of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{CH}_3)$  (**1b**) in  $\text{C}_6\text{D}_6$ .

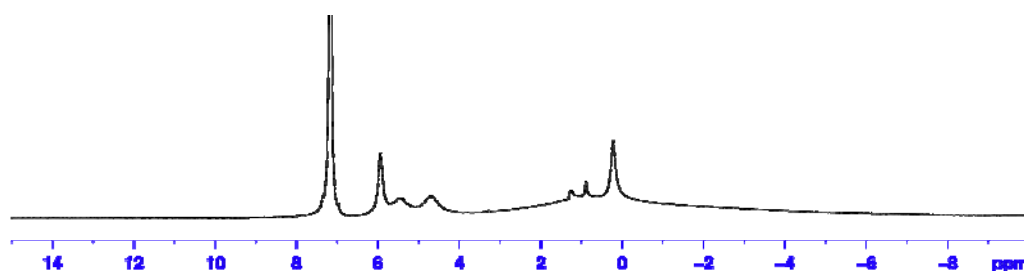


Figure S3.  $^1\text{H}$ -NMR spectrum of  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{B}(3,5-(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**3**) in  $\text{C}_6\text{D}_6/\text{THF-d}_8$  (5/1).

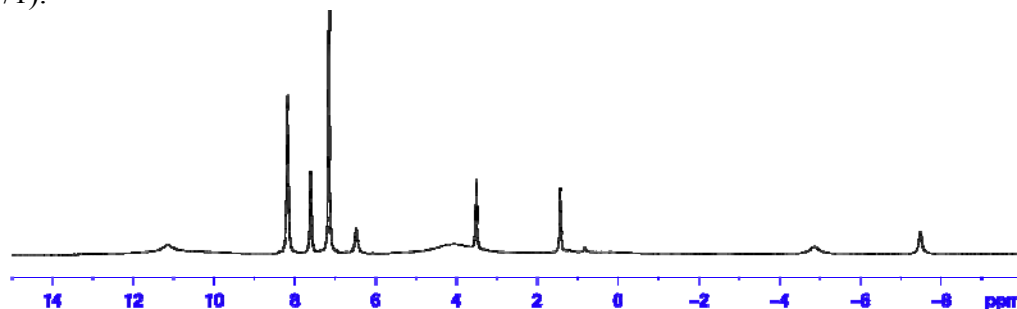


Figure S4.  $^1\text{H}$ -NMR spectrum of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{Cl})$  in  $\text{C}_6\text{D}_6$ .

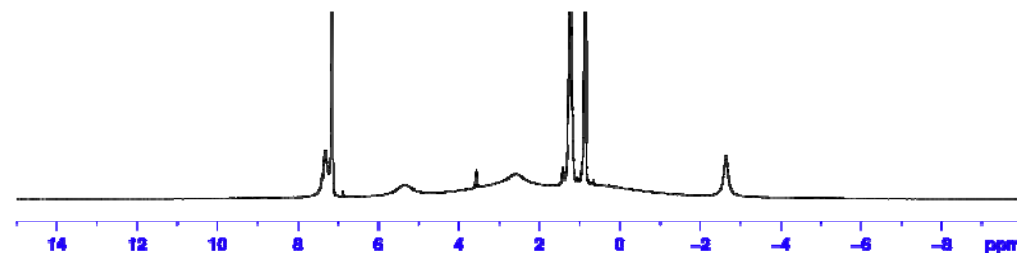


Figure S5.  $^1\text{H}$ -NMR spectrum of  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)]$  (**4b**) in  $\text{C}_6\text{D}_6$ .

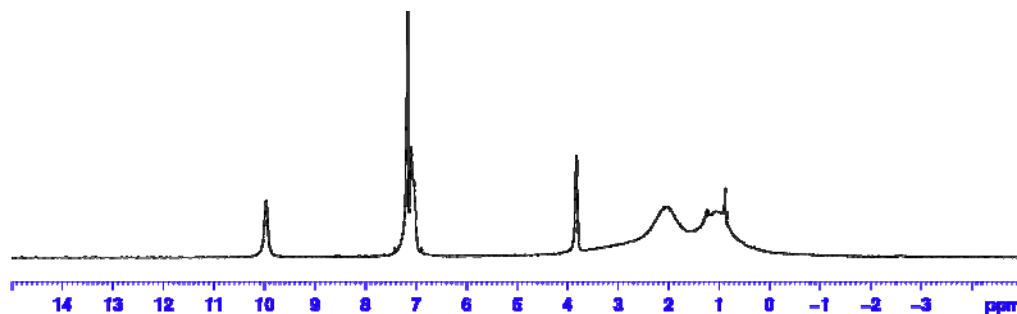


Figure S6.  $^1\text{H}$ -NMR spectrum of  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(\text{THF})_3]$  (**5**) in  $\text{THF-d}_8$ .

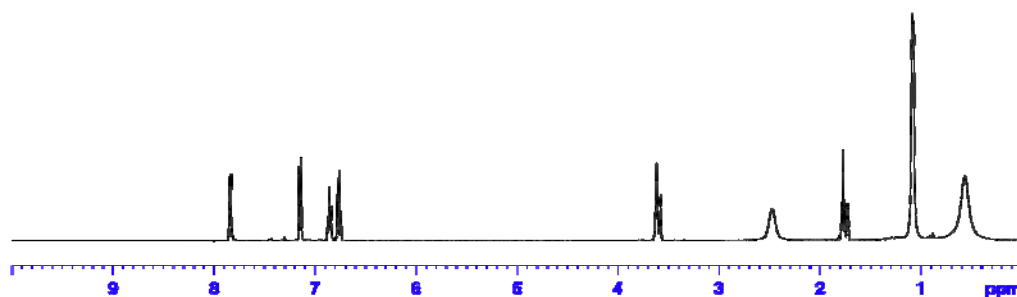


Figure S7.  $^{31}\text{P}$ -NMR spectrum of  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(\text{THF})_3]$  (**5**) in  $\text{THF-d}_8$  at  $-70^\circ\text{C}$ .

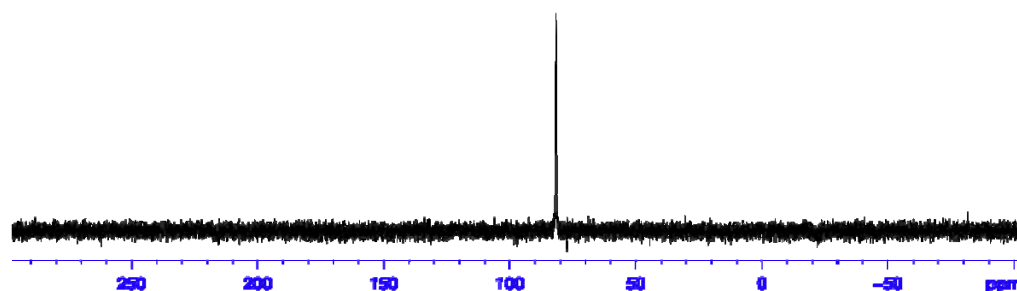


Figure S8.  $^{15}\text{N}$ -NMR spectrum of  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(\text{THF})_3]$  (**5**) in  $\text{THF-d}_8$ .

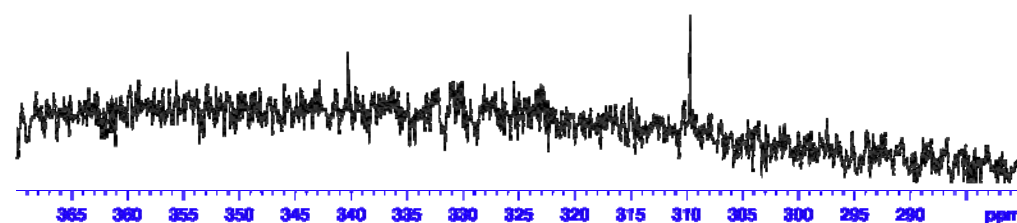




Figure S9.  $^1\text{H}$ -NMR spectrum of  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(12\text{-C-4})_2]$  (**5'**) in  $\text{THF-d}_8$ .

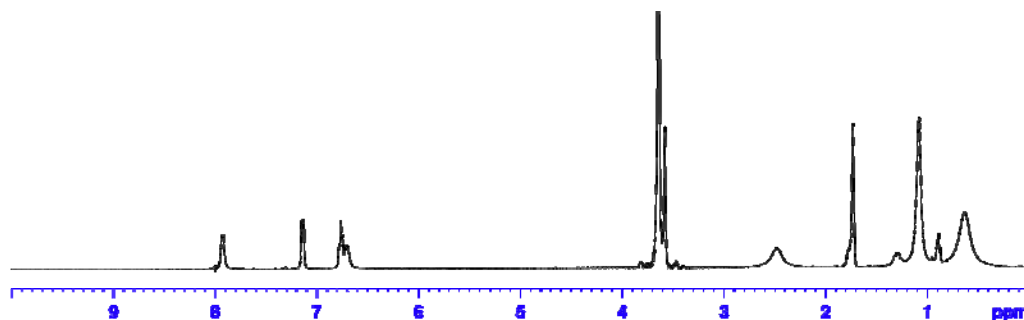


Figure S10.  $^{31}\text{P}$ -NMR spectrum of  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(12\text{-C-4})_2]$  (**5'**) in  $\text{THF-d}_8$  at  $-70^\circ\text{C}$ .

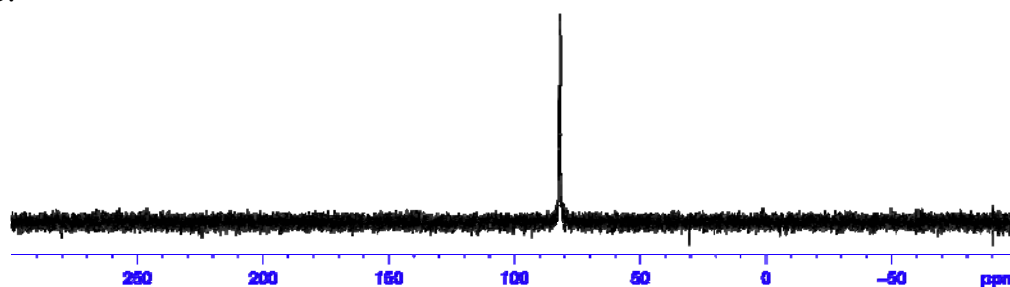


Figure S11.  $^{15}\text{N}$ -NMR spectrum of  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(12\text{-C-4})_2]$  (**5'**) in  $\text{THF-d}_8$ .

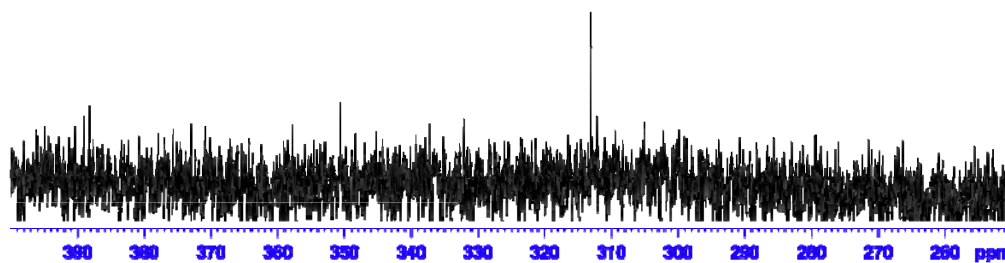


Figure S12.  $^1\text{H}$ -NMR spectrum of  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6a•OTf**) in  $\text{THF-d}_8$ .

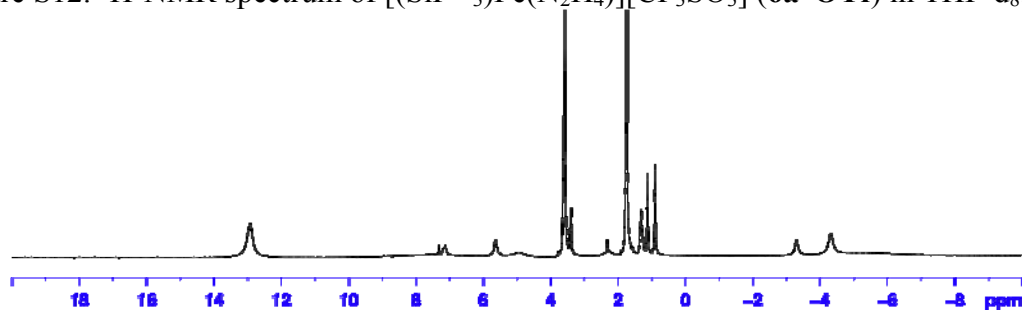


Figure S13.  $^1\text{H}$ -NMR spectrum of  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**6a•B(ArF)**) in  $\text{C}_6\text{D}_6/\text{THF-d}_8$  (5/1).

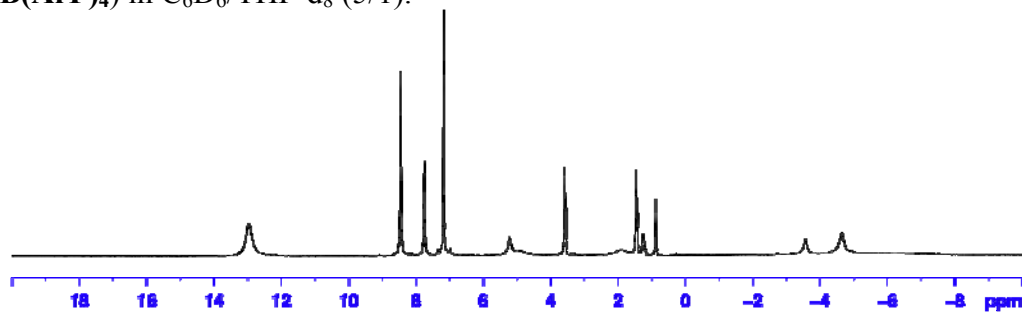


Figure S14.  $^1\text{H}$ -NMR spectrum of  $[(\text{SiP}^{\text{Pr}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**6b•B(ArF)**) in  $\text{C}_6\text{D}_6/\text{THF-d}_8$  (5/1).

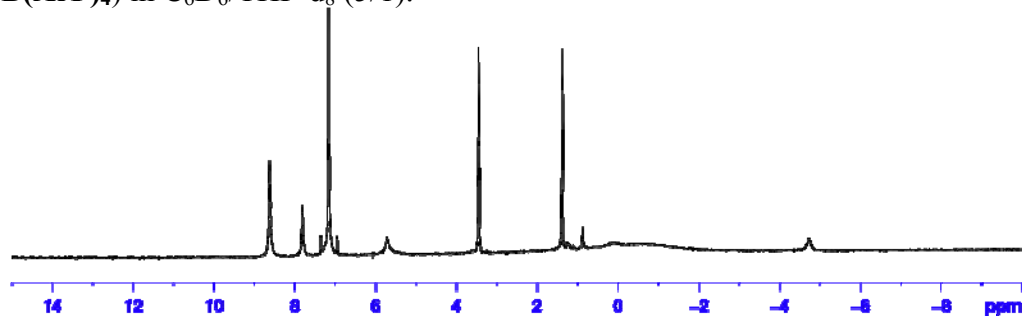


Figure S15.  $^1\text{H}$ -NMR spectrum of  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7a**) in  $\text{C}_6\text{D}_6/\text{THF-d}_8$  (5/1).

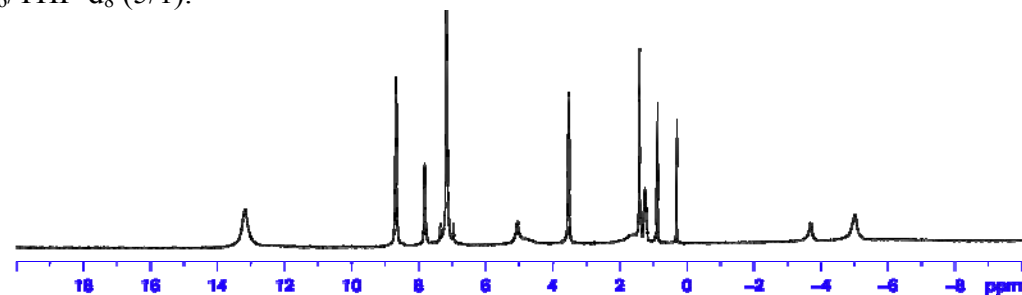


Figure S16.  $^1\text{H}$ -NMR spectrum of  $[(\text{SiP}^{\text{iPr}})_3\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7b**) in  $\text{C}_6\text{D}_6/\text{THF-d}_8$  (5/1).

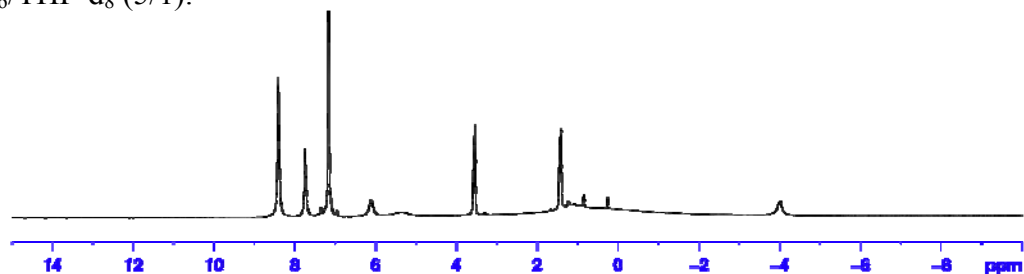


Figure S17.  $^1\text{H}$ -NMR spectrum of  $(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)$  (**9a**) in  $\text{C}_6\text{D}_6/\text{THF-d}_8$  (5/1).

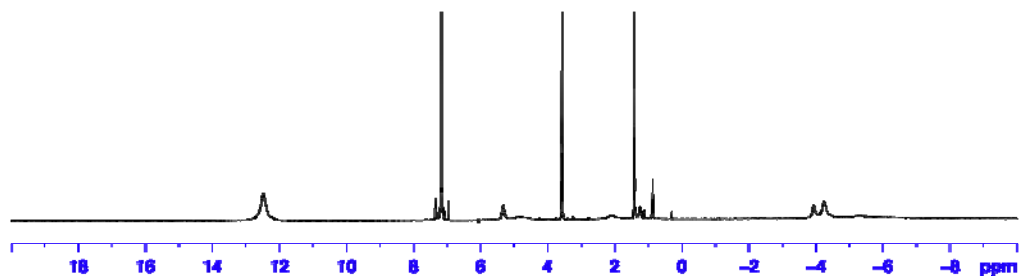


Figure S18.  $^1\text{H}$ -NMR spectrum of  $(\text{SiP}^{\text{iPr}})_3\text{Fe}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)$  (**9b**) in  $\text{C}_6\text{D}_6/\text{THF-d}_8$  (5/1).

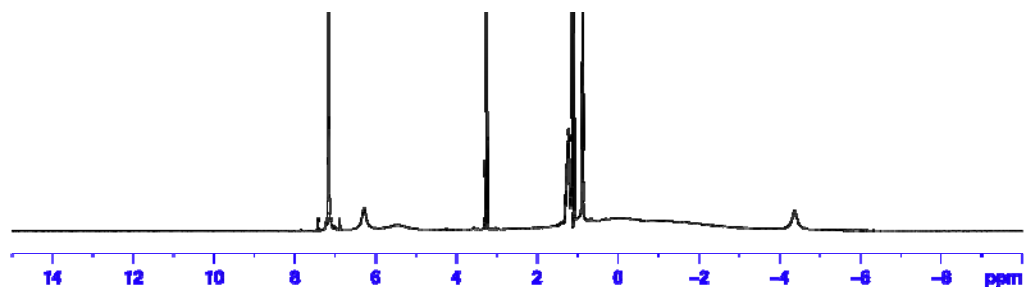


Figure S19.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{TMS})$  (**12**) measured at room temperature.

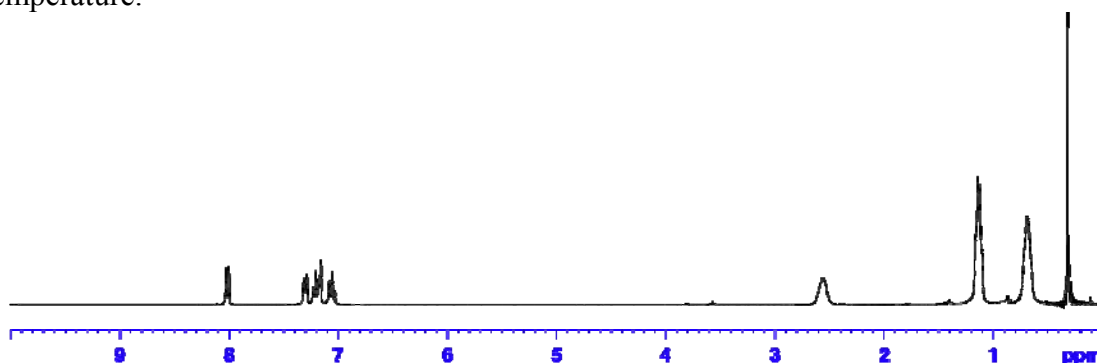


Figure S20.  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{TMS})$  (**12**) measured at room temperature.

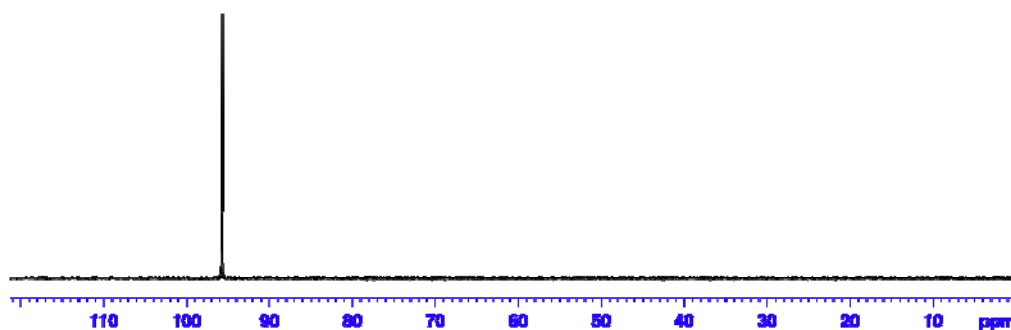


Figure S21.  $^{29}\text{Si}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(^{14}\text{N}_2\text{TMS})$  (**12**, top) and  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(^{15}\text{N}_2\text{TMS})$  (**12**- $^{15}\text{N}_2$ , bottom) measured at room temperature.

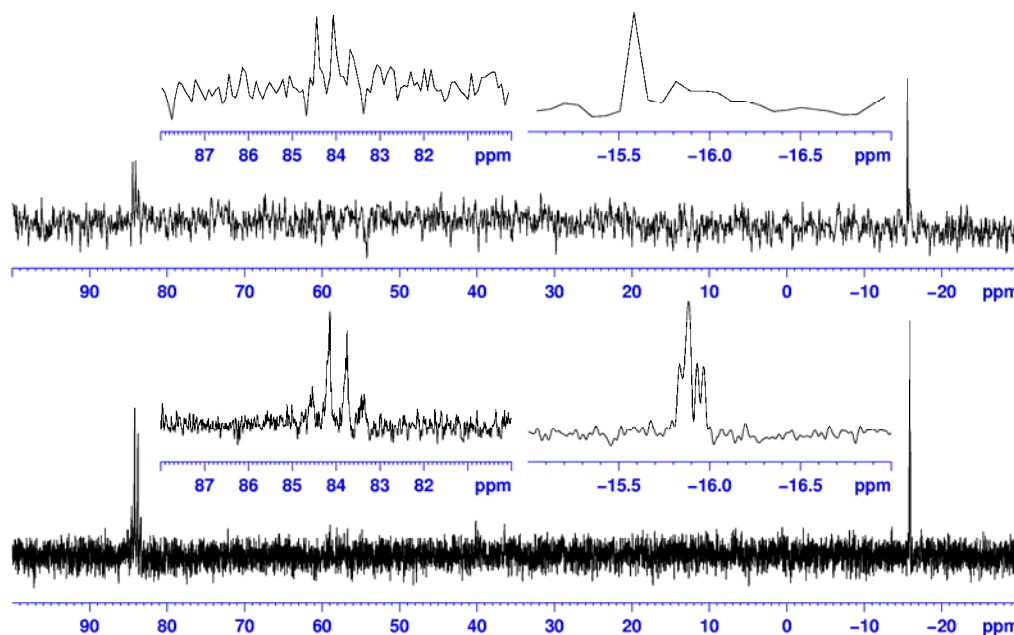


Figure S22.  $^{15}\text{N}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)_3\text{Fe}(^{15}\text{N}_2\text{TMS})$  (**12- $^{15}\text{N}_2$** ) measured at room temperature.

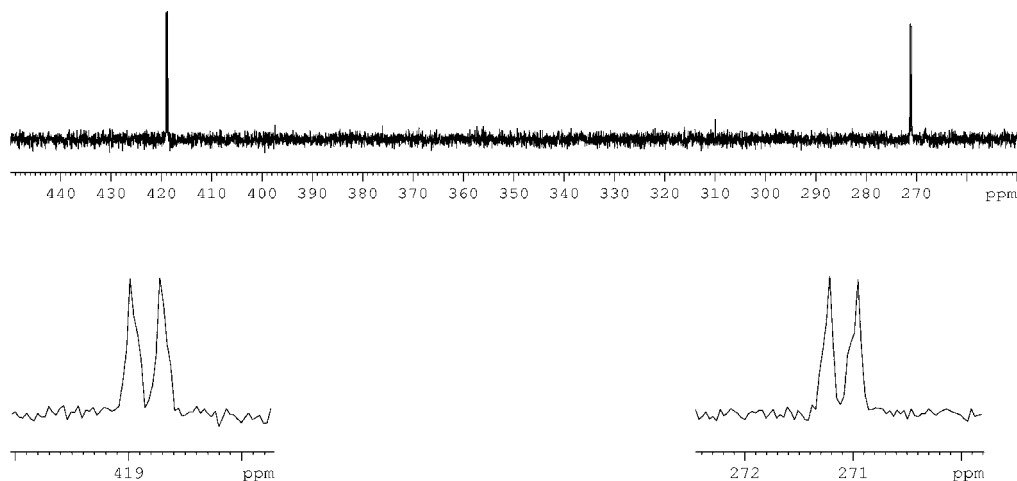


Figure S23.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)_3\text{Fe}(\text{N}_2\text{Si}i\text{Pr}_3)$  measured at room temperature.

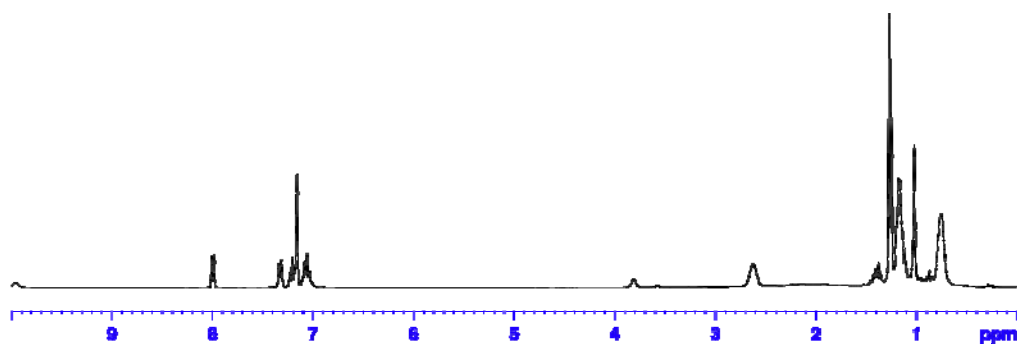


Figure S24.  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)_3\text{Fe}(\text{N}_2\text{Si}i\text{Pr}_3)$  measured at room temperature.

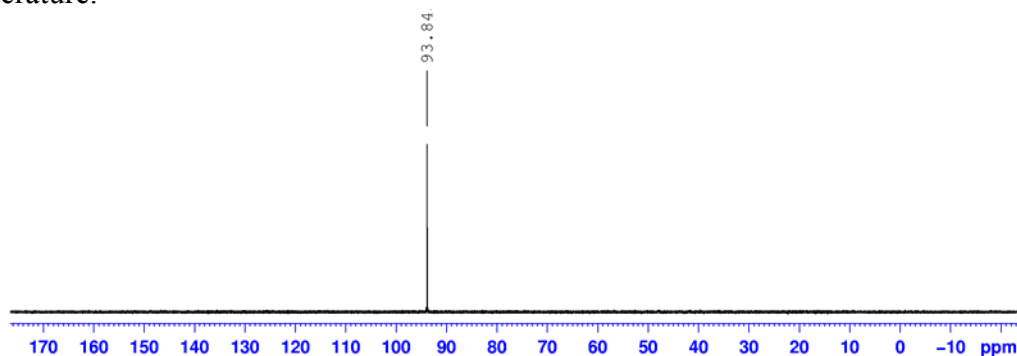


Figure S25.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{SiPh}_3)$  measured at room temperature.

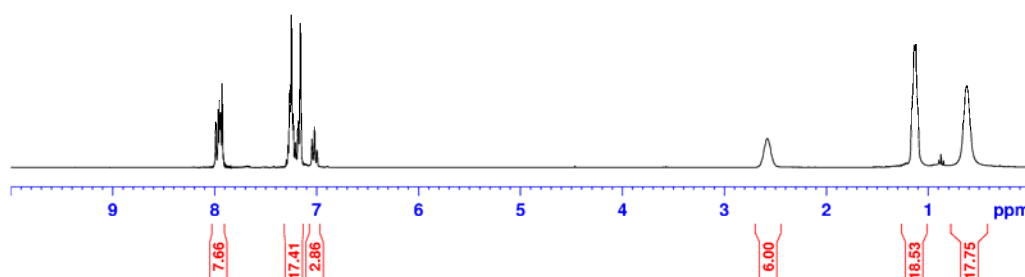


Figure S26.  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{SiPh}_3)$  measured at room temperature.

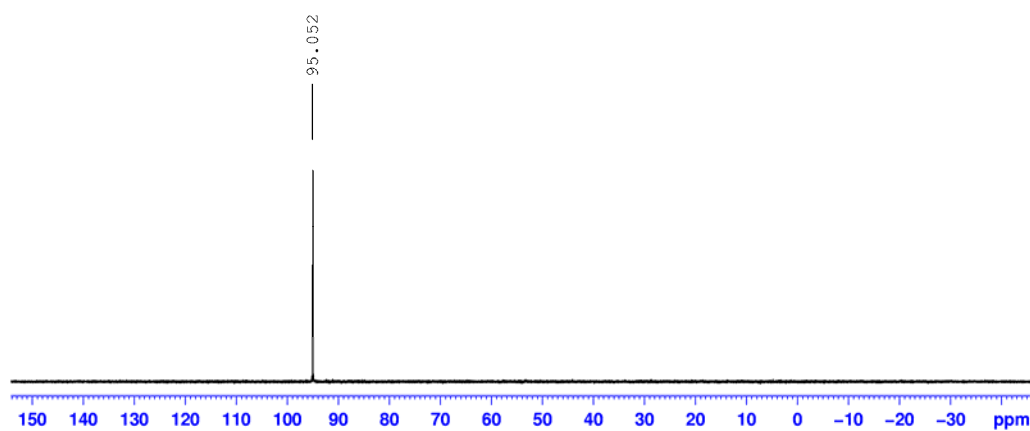


Figure S27.  $^{29}\text{Si}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{SiPh}_3)$  (top) and  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(^{15}\text{N}_2\text{SiPh}_3)$  (bottom) measured at room temperature.

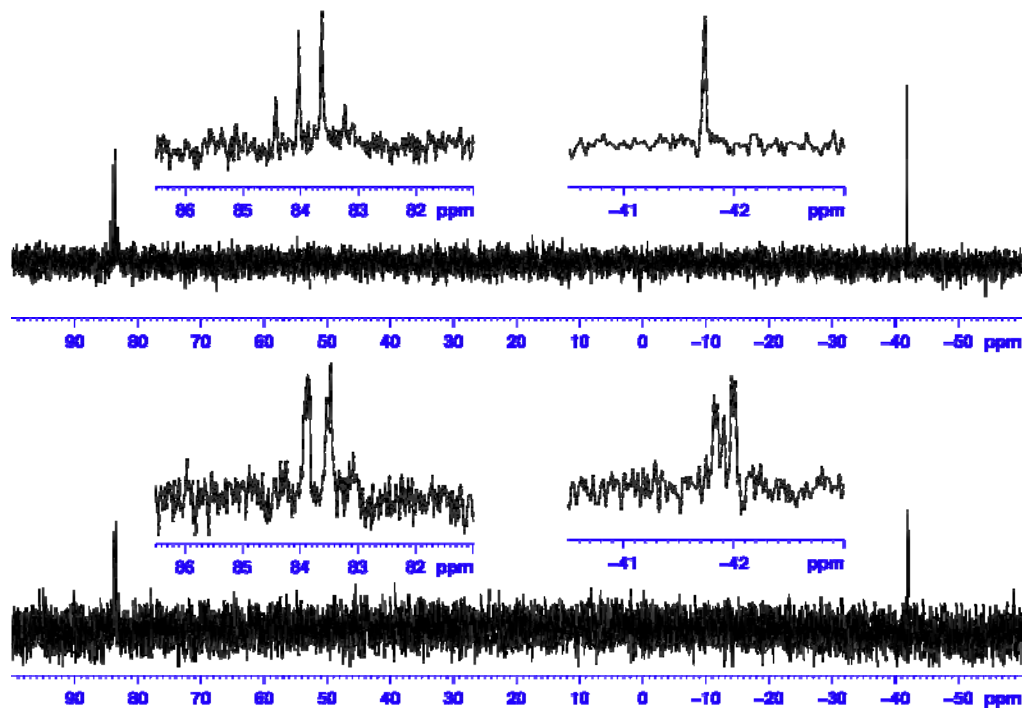


Figure S28.  $^{15}\text{N}$ -NMR ( $\text{C}_6\text{D}_6$ , ppm) of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(^{15}\text{N}_2\text{SiPh}_3)$  measured at room temperature.

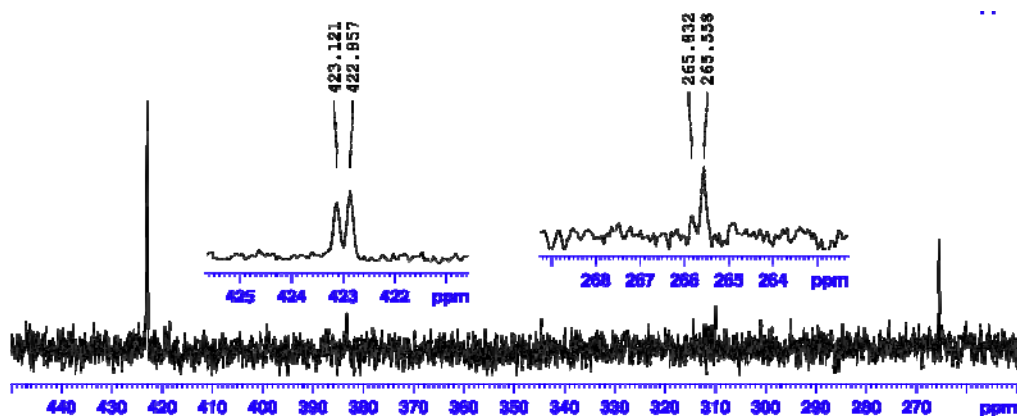


Figure S29. IR spectra of  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{CH}_3)$  (**1a**) and  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{CH}_3)$  (**1b**) (KBr pellet).

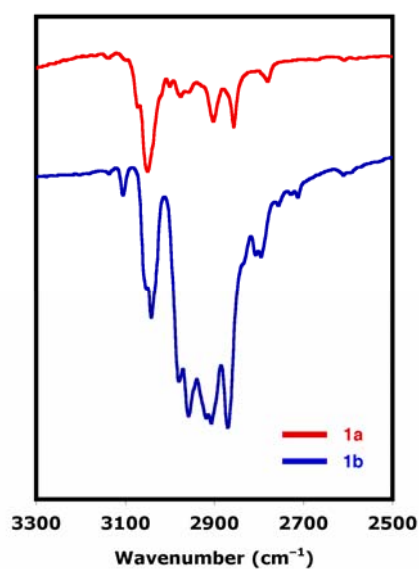


Figure S30. Cyclic voltammograms of **1a** (red;  $-0.52$  and  $-2.25$  V) and **1b** (blue;  $-0.85$ ,  $-2.67$  V) in tetrahydrofuran at RT.

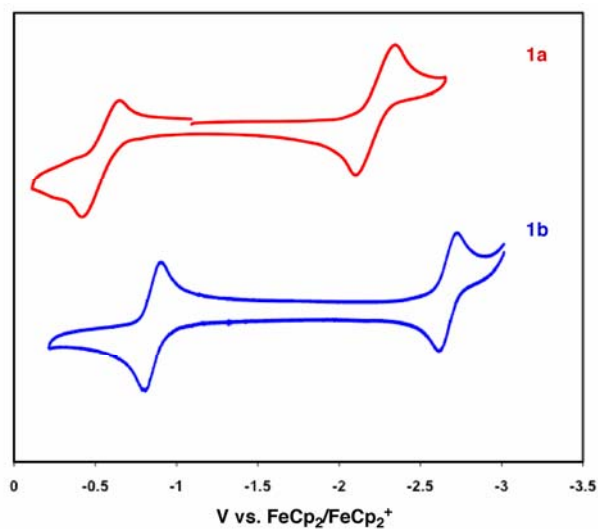




Figure S31. X-ray structure for  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{CH}_3)$  (**1a**). All hydrogen atoms are omitted for clarity.

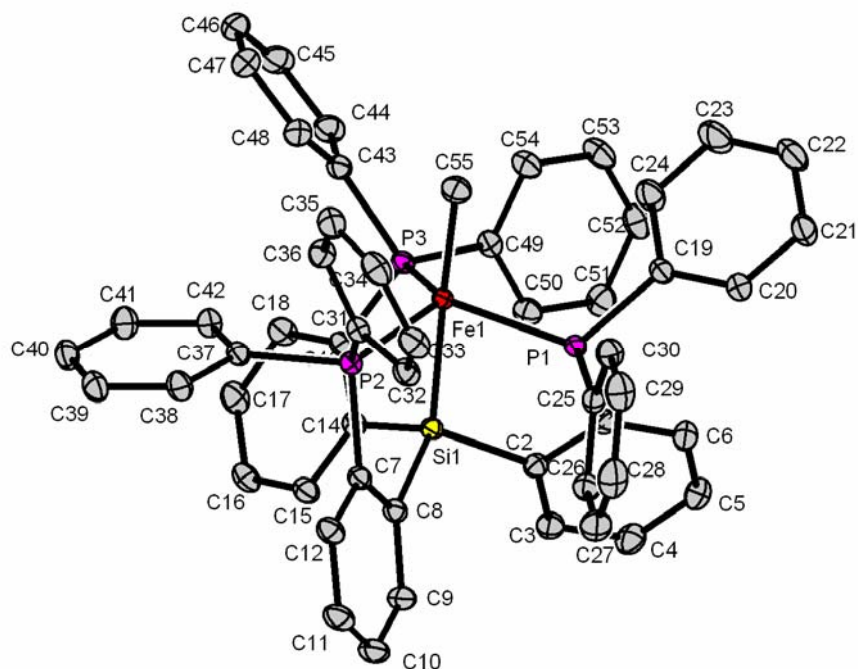


Figure S32. X-ray structure for  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{CH}_3)$  (**1b**). All hydrogen atoms are omitted for clarity.

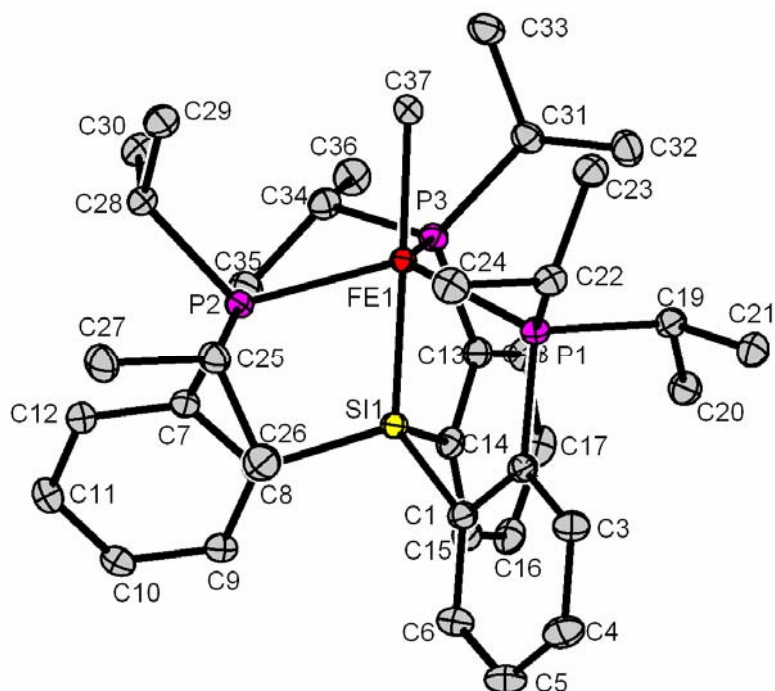


Figure S33. UV-Vis spectrum of  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**3**, green spectra: 420 {sh}, 500 {270}, 610 {115}, 755 {160}) in THF at room temperature. After bubbling argon through the solution to afford  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{THF})][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**2b**, red spectra: 455 {830}, 500 {780}, 1010 {50}). The spectra were measured at 10 sec intervals.

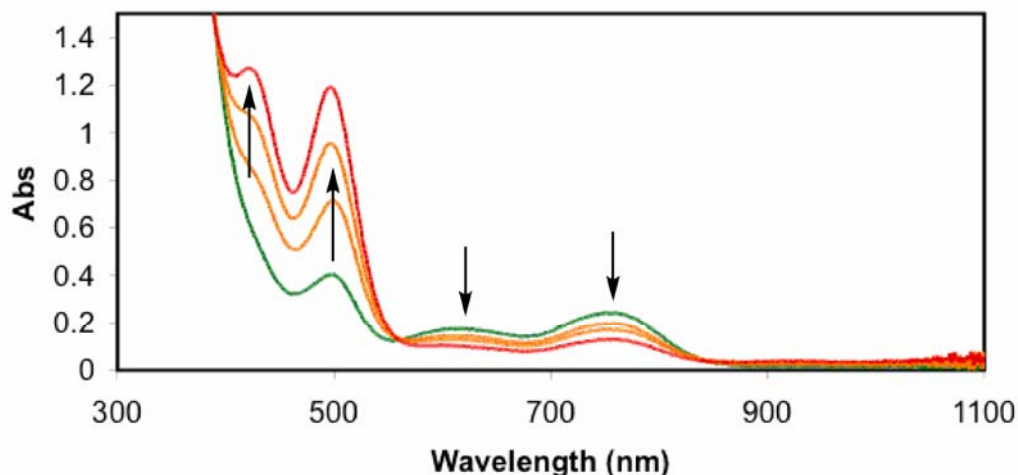


Figure S34. X-ray structure for  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**3**). All hydrogen atoms are omitted for clarity.

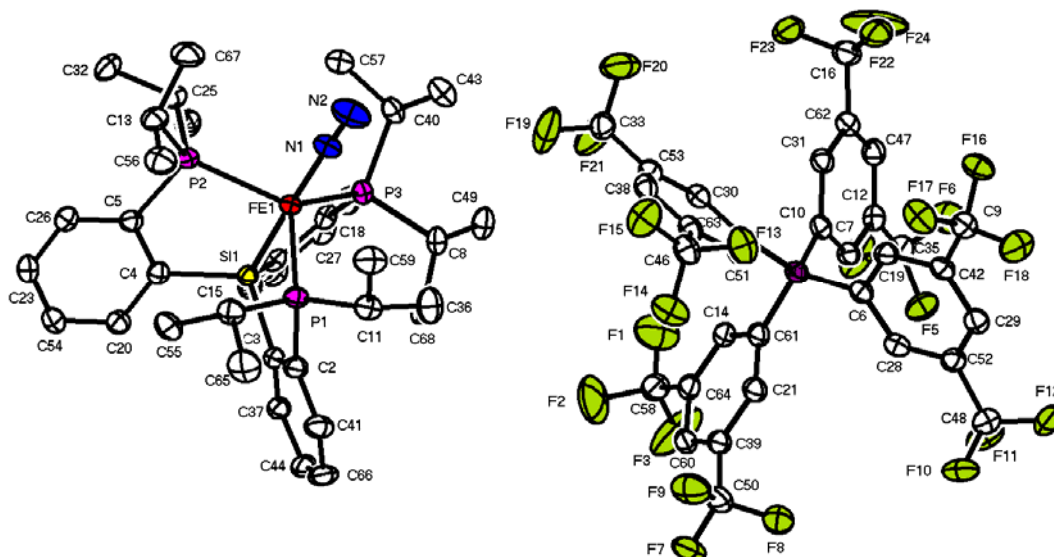


Figure S35. X-ray structure for  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)$  (**4b**). Hydrogen atoms are omitted for clarity. Note: The previously reported solid-state structure of this complex contained an ca. 4%  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{Cl})$ .<sup>xiii</sup> The structure reported herein is of higher quality.

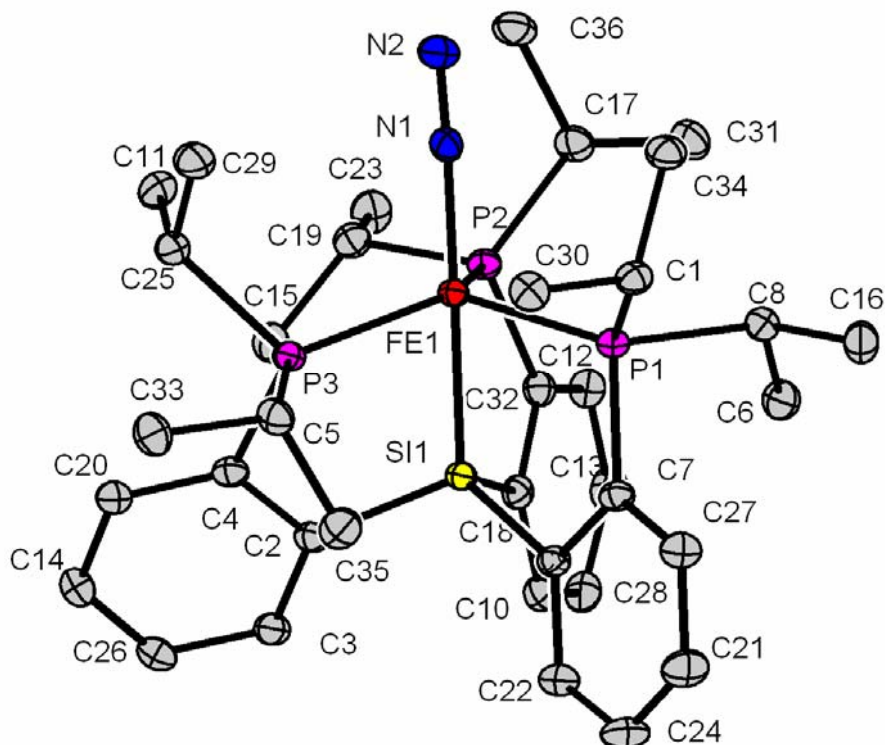


Figure S36. X-ray structure for  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(\text{THF})_3]$  (**5**). Hydrogen atoms are omitted for clarity.

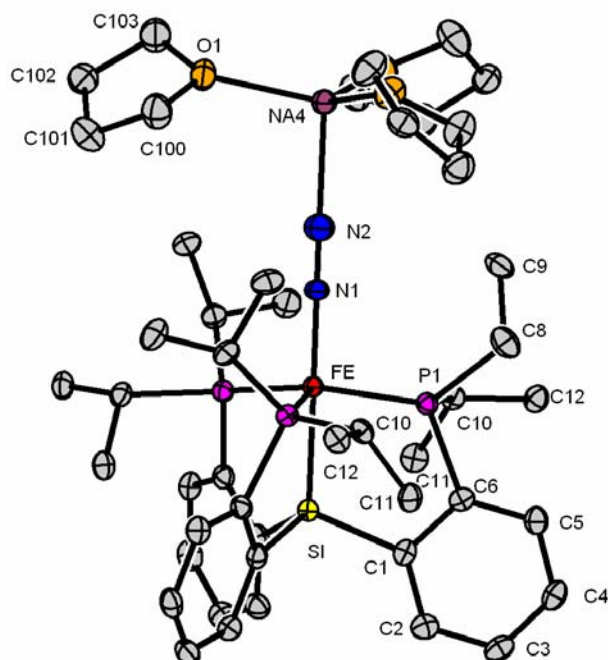


Figure S37.  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(12\text{-C-4})_2]$  (**5'**). Three tetrahydrofuran solvent molecules and C-H hydrogens have been omitted for clarity. One of the crown ethers was disordered over three distinct positions. For clarity, only one component is shown.

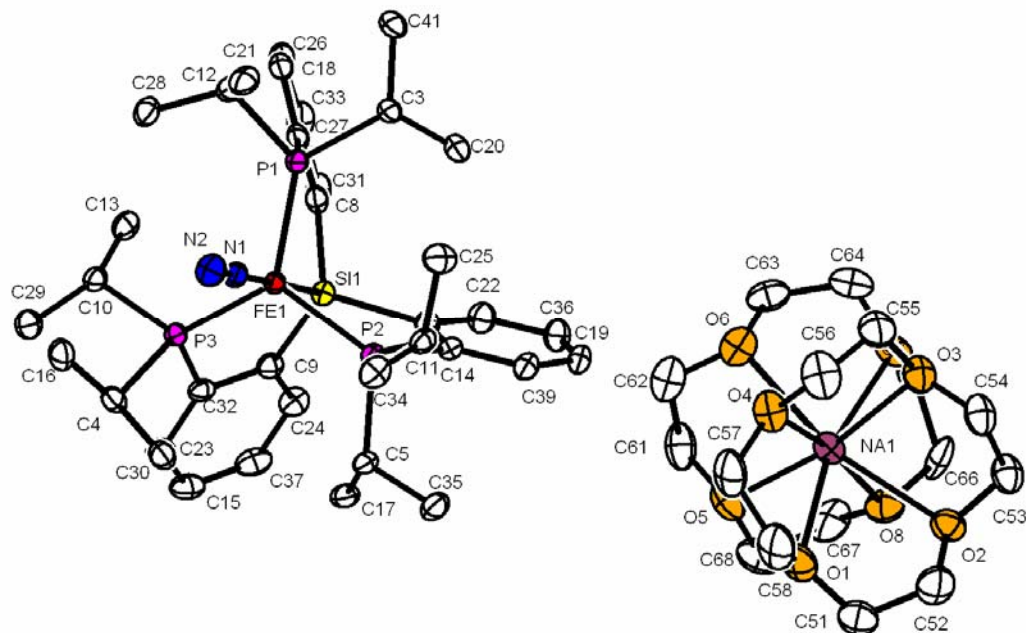


Figure S38. IR spectra of hydrazine adduct complexes. Left:  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6a•OTf**): 3359, 3311, 3277, 3223, 3161  $\text{cm}^{-1}$ ,  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6b•OTf**): 3390, 3299, 3274, 3230, 3155  $\text{cm}^{-1}$ . Right:  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**6a•B(ArF)\_4**): 3400, 3357, 3325, 3273, 3252  $\text{cm}^{-1}$ ,  $[(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**6b•B(ArF)\_4**): 3407, 3324, 3260  $\text{cm}^{-1}$ .

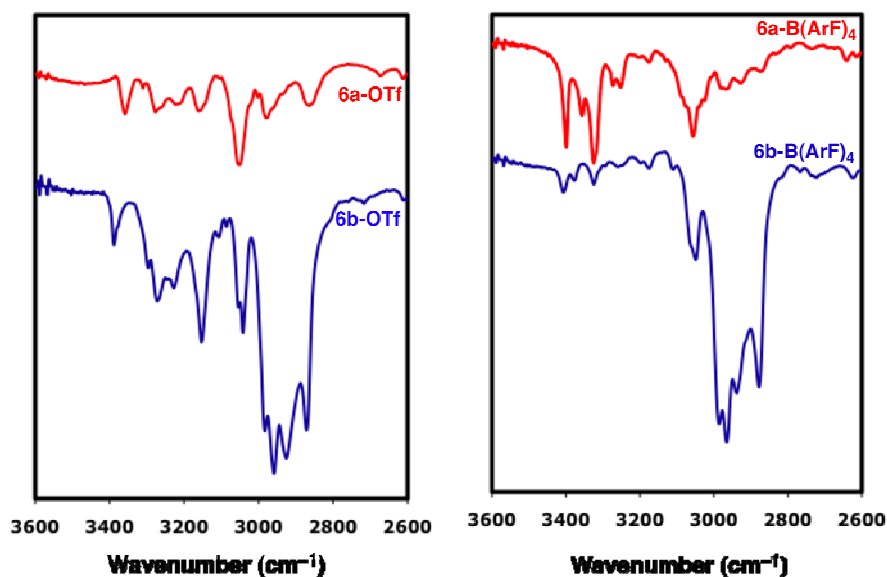


Figure S39. X-ray structure for  $[(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6a•OTf**). Hydrogen atoms, the second molecule of the asymmetric unit, and two tetrahydrofuran co-solvent molecules are omitted for clarity.

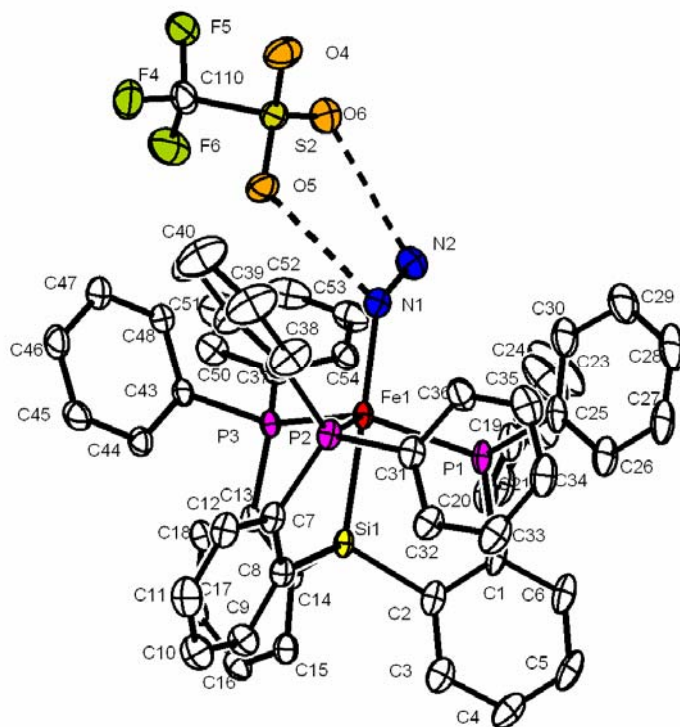


Figure S40. X-ray structure for  $[(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{H}_4)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**6a•B(ArF)<sub>4</sub>**). Hydrogen atoms and the second molecule of the asymmetric unit are omitted for clarity.

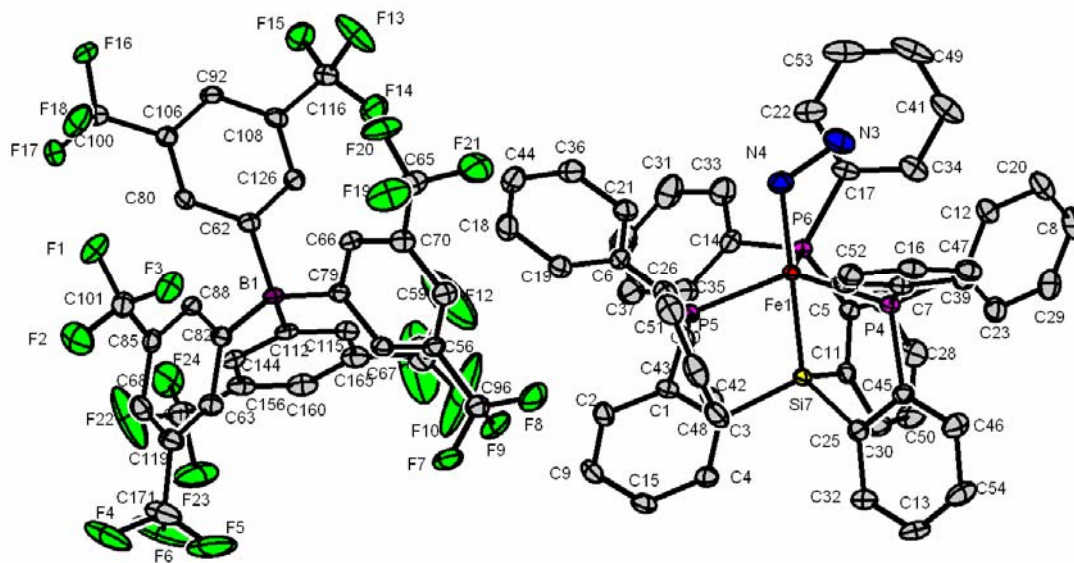




Figure S41. X-ray structure for  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2\text{H}_4)][\text{CF}_3\text{SO}_3]$  (**6b•OTf**). All C-H hydrogens are omitted for clarity. N-H hydrogens were located on the Fourier difference map and their positions were freely refined.

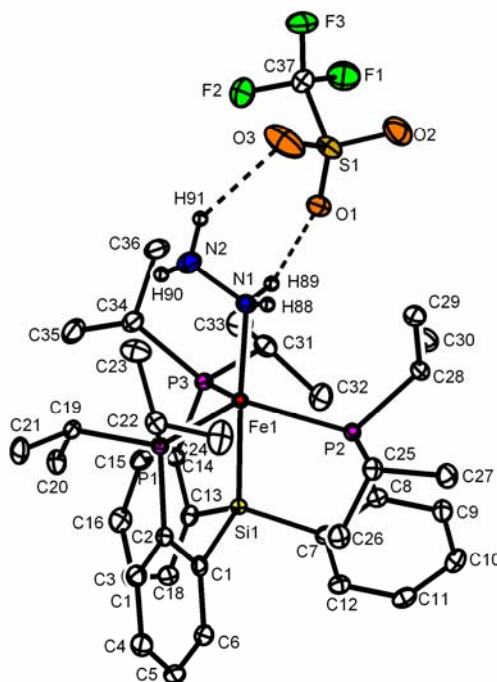


Figure S42. IR spectra for: Left:  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7a**): 3366, 3348, 3278  $\text{cm}^{-1}$ ,  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7b**): 3377, 3293, 3199  $\text{cm}^{-1}$ ; Right:  $\text{N}_2\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3$ : 3387, 3322, 3298, 3140  $\text{cm}^{-1}$ ,  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)$  (**9a**): 3395, 3372, 3326, 3273, 3183  $\text{cm}^{-1}$ ,  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)$  (**9b**): 3433, 3291, 3245  $\text{cm}^{-1}$ .

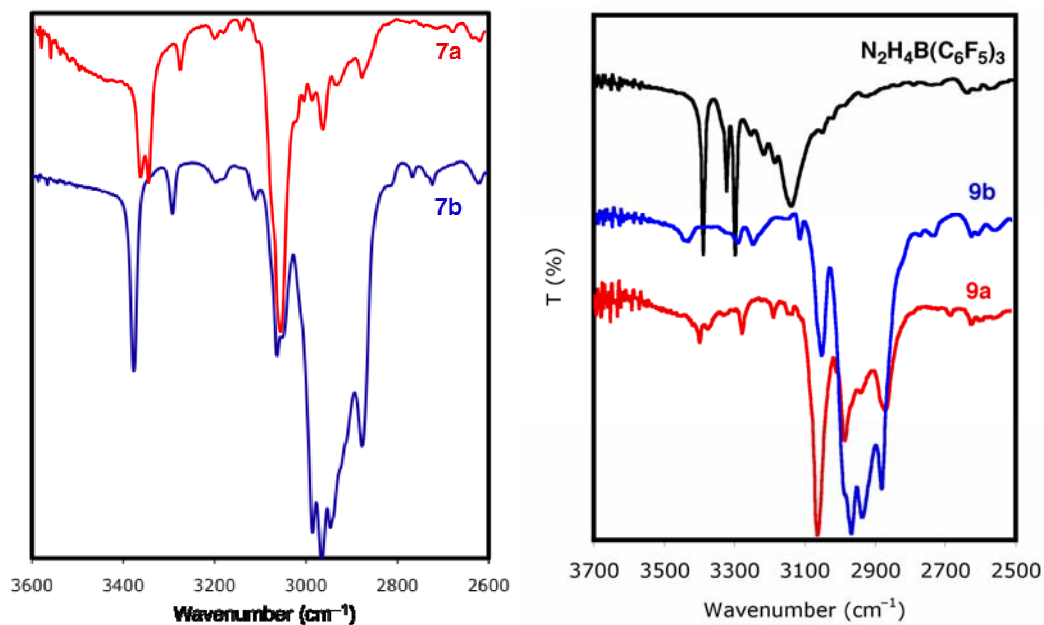


Figure S43. X-ray structure for  $[(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7a**). Three tetrahydrofuran solvent molecules and all C-H hydrogens are omitted for clarity.

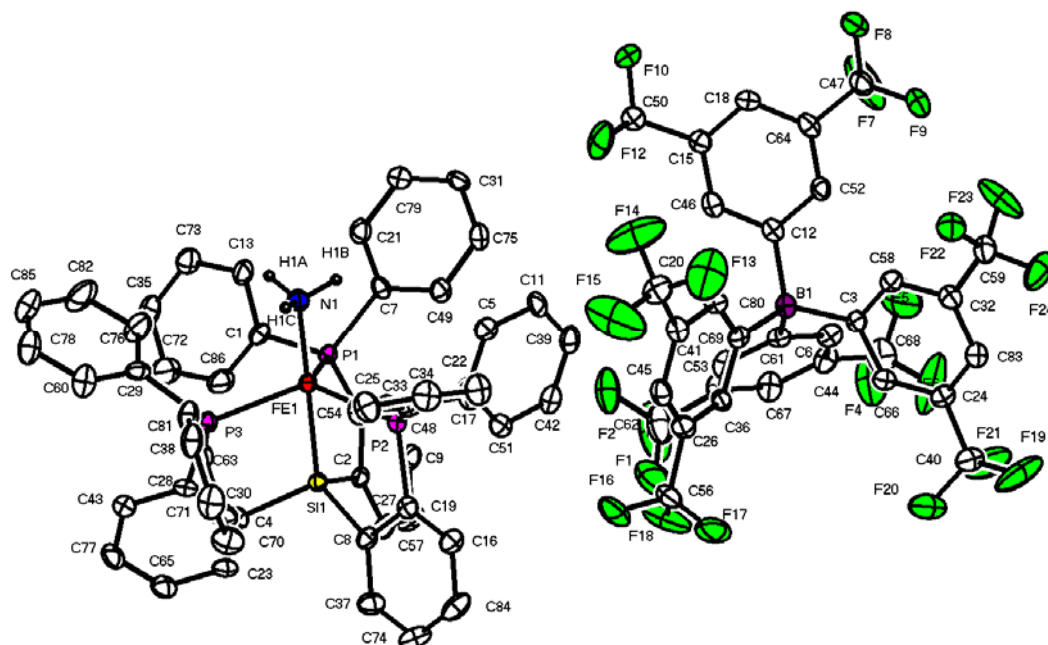


Figure S44. X-ray structure for  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{NH}_3)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**7b**). All C-H hydrogens are omitted for clarity.

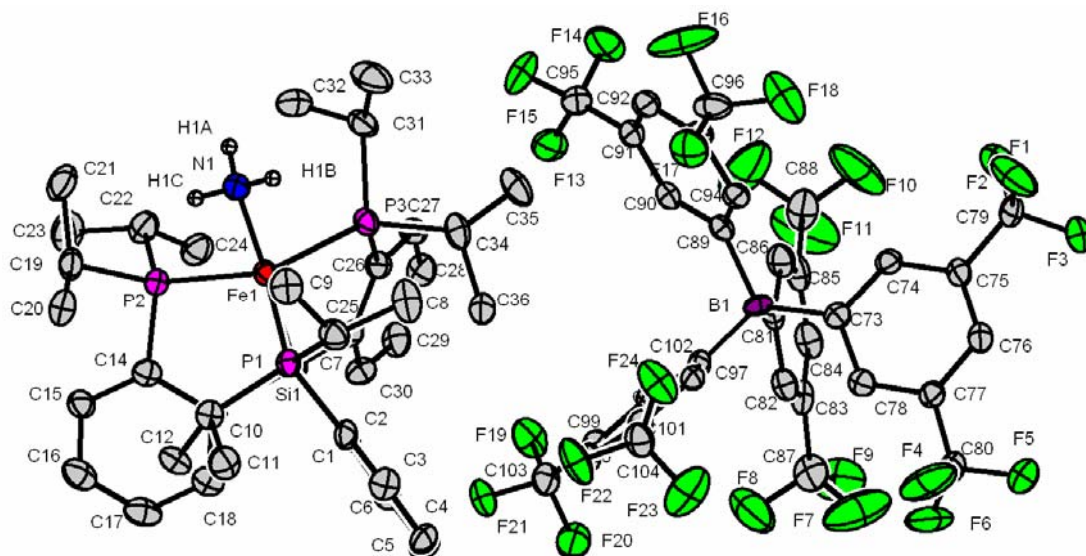


Figure S45. X-ray structure for  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{OAc})$ . One benzene molecule of co-crystallization, and all hydrogen atoms are omitted for clarity.

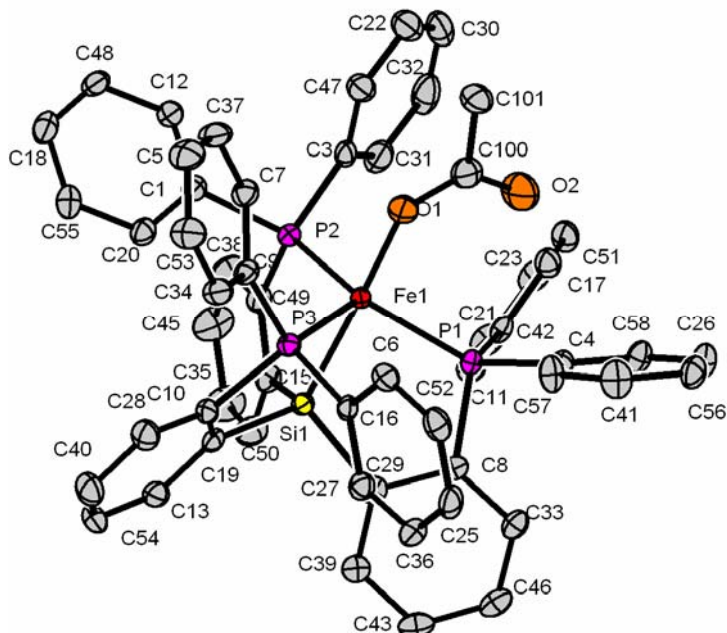


Figure S46. X-ray structure for  $\{\text{[Si}(o\text{-C}_6\text{H}_4\text{PPh}_2)_2(o\text{-C}_6\text{H}_4\text{P}(=\text{NH})\text{Ph}_2)]\text{Fe}(\text{NH}_3)\}\{\text{CF}_3\text{SO}_3\}$  (**8**). Solvent molecules of co-crystallization (one THF and one benzene) and all C-H hydrogens have been omitted for clarity.

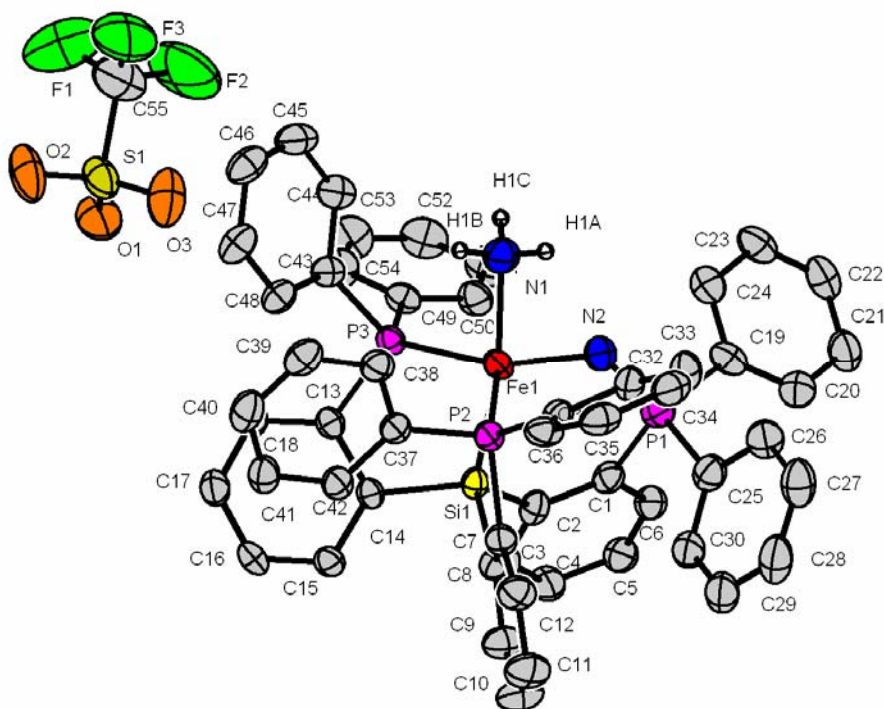




Figure S47. X-ray structure for  $\text{N}_2\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3$ . N-H hydrogens were located on the Fourier difference map and their positions were freely refined.

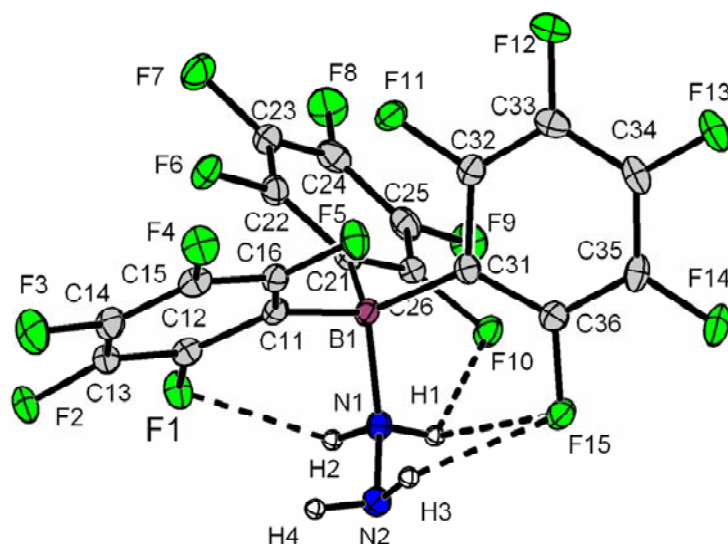


Figure S48. X-ray structure for  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)$  (**9a**). One benzene molecule and all hydrogen atoms that are not involved in hydrogen bonds are omitted for clarity. N-H hydrogens were located on the Fourier difference map and their positions were freely refined.

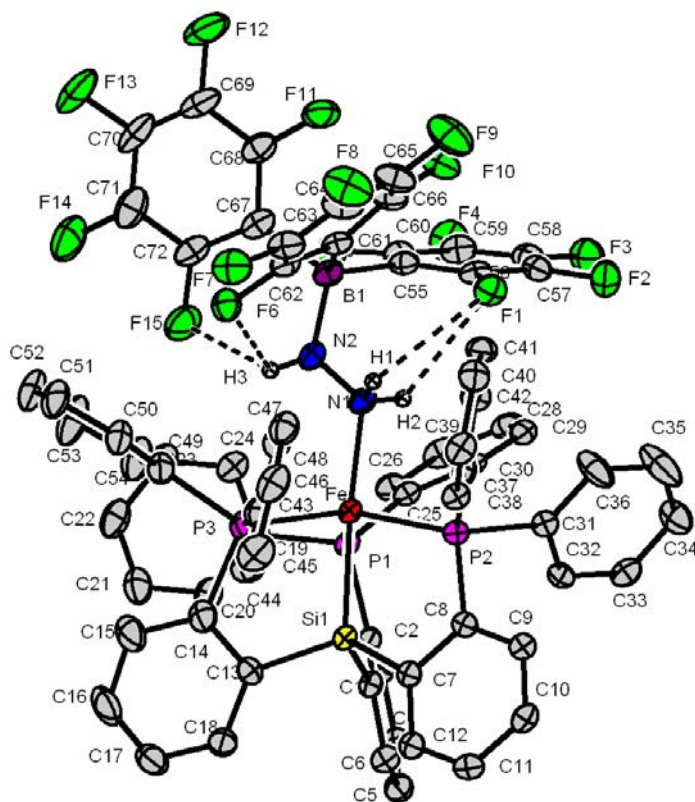


Figure S49. X-ray structure for  $[(\text{SiP}^{\text{iPr}}_3)\text{Fe}^{\text{II}}(\text{N}_2\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3)]$  (**9b**). One pentane and one benzene molecules and all hydrogen atoms are omitted for clarity. N-H hydrogens were located on the Fourier difference map and their positions were freely refined.

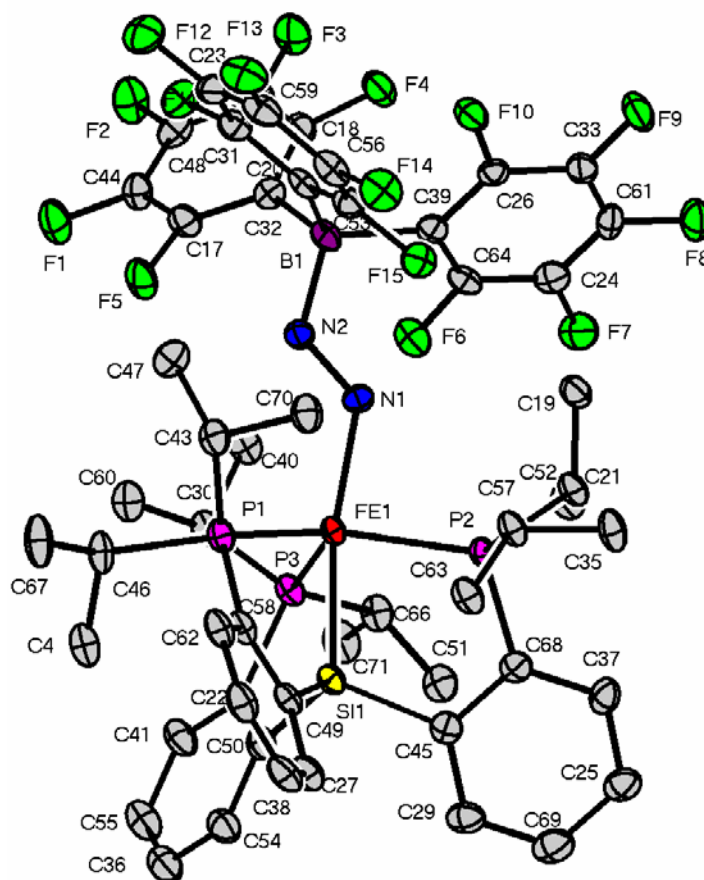


Table S1. Selected bond distances and angles for **6a**•B(ArF)<sub>4</sub>, **6a**•OTf, **6b**•OTf, N<sub>2</sub>H<sub>4</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, **9a** and **9b** (Å and °).

	d(N-N)	d(Fe-N)	d(N-B)	∠FeNN	∠NNB	τ
<b>6a</b> •B(ArF) <sub>4</sub>	1.429(3)	2.074(2)	–	115.8(2)	–	0.84
	1.450(3)	2.076(2)	–	116.3(2)	–	0.93
<b>6a</b> •OTf	1.468(6)	2.051(4)	–	118.7(3)	–	0.94
	1.473(7)	2.061(5)	–	116.4(4)	–	0.90
<b>6b</b> •OTf	1.461(2)	2.076(2)	–	124.2(1)	–	0.96
<b>N<sub>2</sub>H<sub>4</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub></b>	1.464(2)	–	1.632(2)	–	120.3(1)	–
<b>9a</b>	1.449(4)	2.061(3)	1.544(5)	122.4(2)	113.2(3)	0.94
<b>9b</b>	1.44(1)	2.088(8)	1.55(1)	128.3(5)	120.8(7)	0.85

Table S2. Hydrogen bonds in N<sub>2</sub>H<sub>4</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and compounds **9a**, **9b** and **6b** (Å and °).

	D-H...A	d(D-H)	d(H...A)	d(D...A)	∠DHA
<b>N<sub>2</sub>H<sub>4</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub></b>	N(1)-H(1)...F(1)	0.91(1)	2.16(2)	2.748(2)	122(1)
	N(1)-H(1)...N(2)#1	0.91(1)	2.18(2)	2.974(2)	144(2)
	N(1)-H(2)...F(1)	0.89(1)	2.27(2)	2.821(2)	120(1)
	N(2)-H(3)...F(2)	0.91(1)	2.36(2)	2.811(2)	111(1)
	N(2)-H(3)...F(4)#2	0.91(1)	2.47(2)	3.059(2)	123(1)
	N(2)-H(3)...F(1)#3	0.91(1)	2.62(2)	3.058(2)	111(1)
	N(2)-H(4)...F(2)#4	0.89(1)	2.54(2)	3.400(2)	162(2)
<b>9a</b>	N1-H2...F1	0.84(6)	2.60(5)	3.074(4)	117(5)
	N2-H3...F6	0.84(4)	2.43(4)	2.868(4)	113(3)
<b>9b</b>	N1-H1...F14	0.86(1)	2.48(1)	3.065(9)	126(1)
	N1-H2...F15	0.90(1)	2.17(1)	2.967(9)	147(1)
	N2-H3...F5	0.88(1)	2.20(1)	2.683(9)	114(9)
<b>6b</b>	N2-H91...O3#1	0.92(3)	2.31(3)	3.112(2)	146(2)
	N1-H89...O1#1	0.86(3)	2.16(3)	2.986(2)	161(2)

Hydrogen bonds with H...A &lt; r(A) + 2.000 Å and &lt;DHA&gt; 110 °.

\* D-H...F hydrogen bond: Short (&lt;2.2), medium (2.2-2.35), and long (2.35-2.55) Å.

Figure S50. X-ray structure for  $(\text{SiP}^{\text{Ph}}_3)\text{Fe}(\text{N}_2\text{C}_6\text{H}_5)$  (**10**). Hydrogen atoms are omitted for clarity.

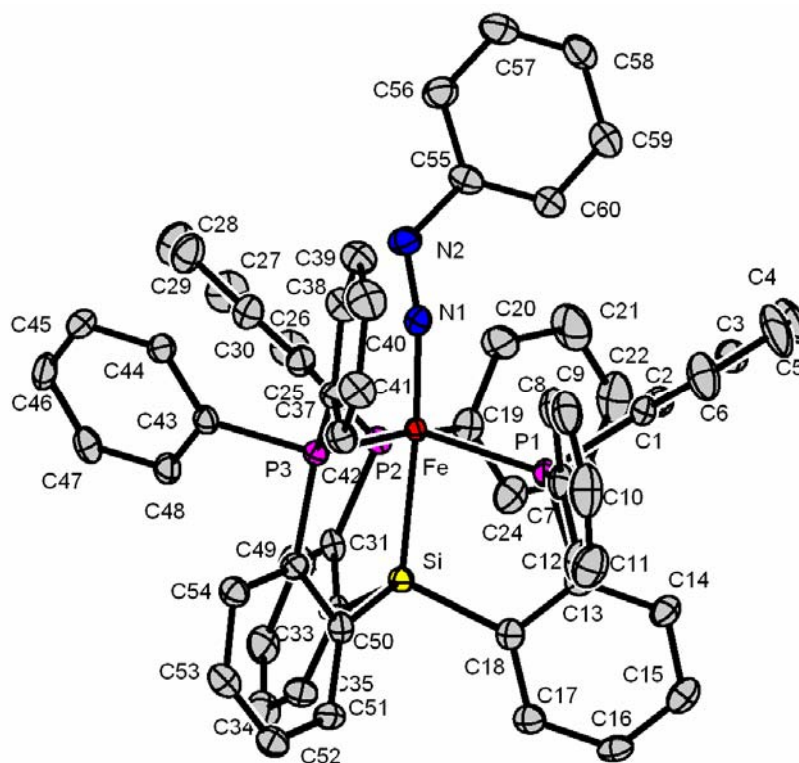


Figure S51. X-ray structure for  $[(\text{SiP}^{\text{Ph}})_3\text{Fe}(\text{N}_2\text{C}_6\text{H}_5)][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$  (**11**). Hydrogen atoms are omitted for clarity.

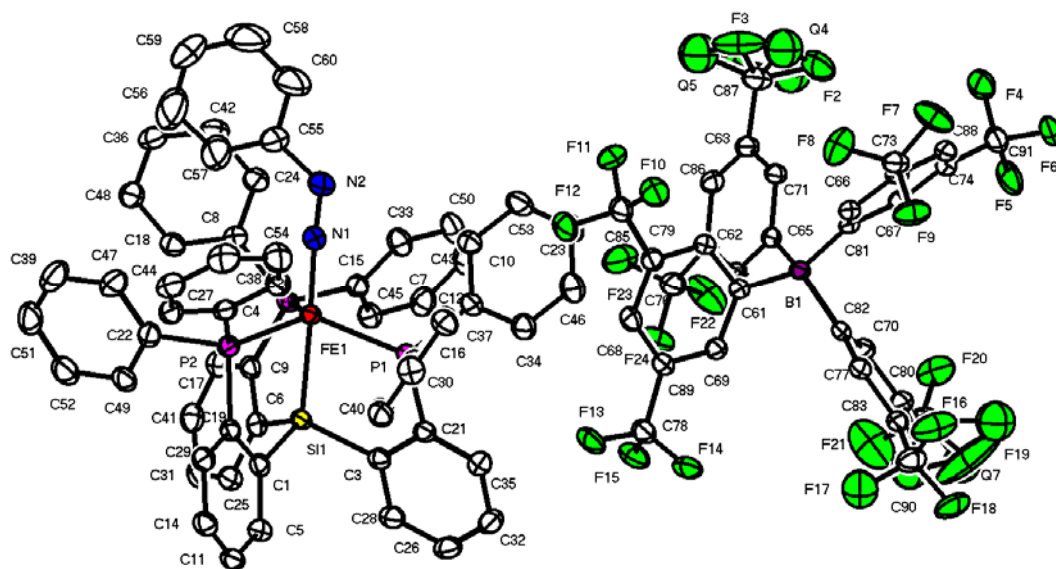


Figure S52. X-ray structure for  $(\text{SiP}^{\text{iPr}}_3)\text{Fe}(\text{N}_2\text{TMS})$  (**12**). Hydrogen atoms are omitted for clarity.

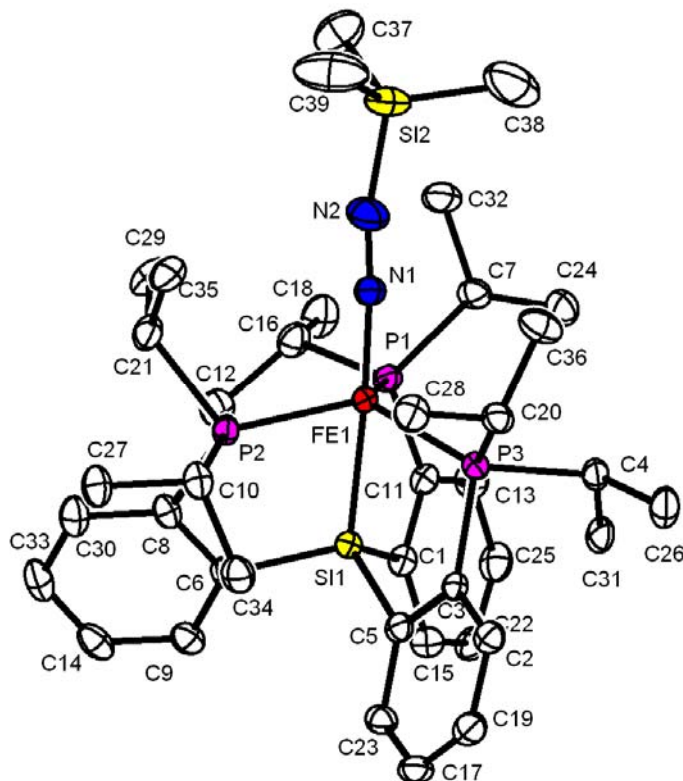
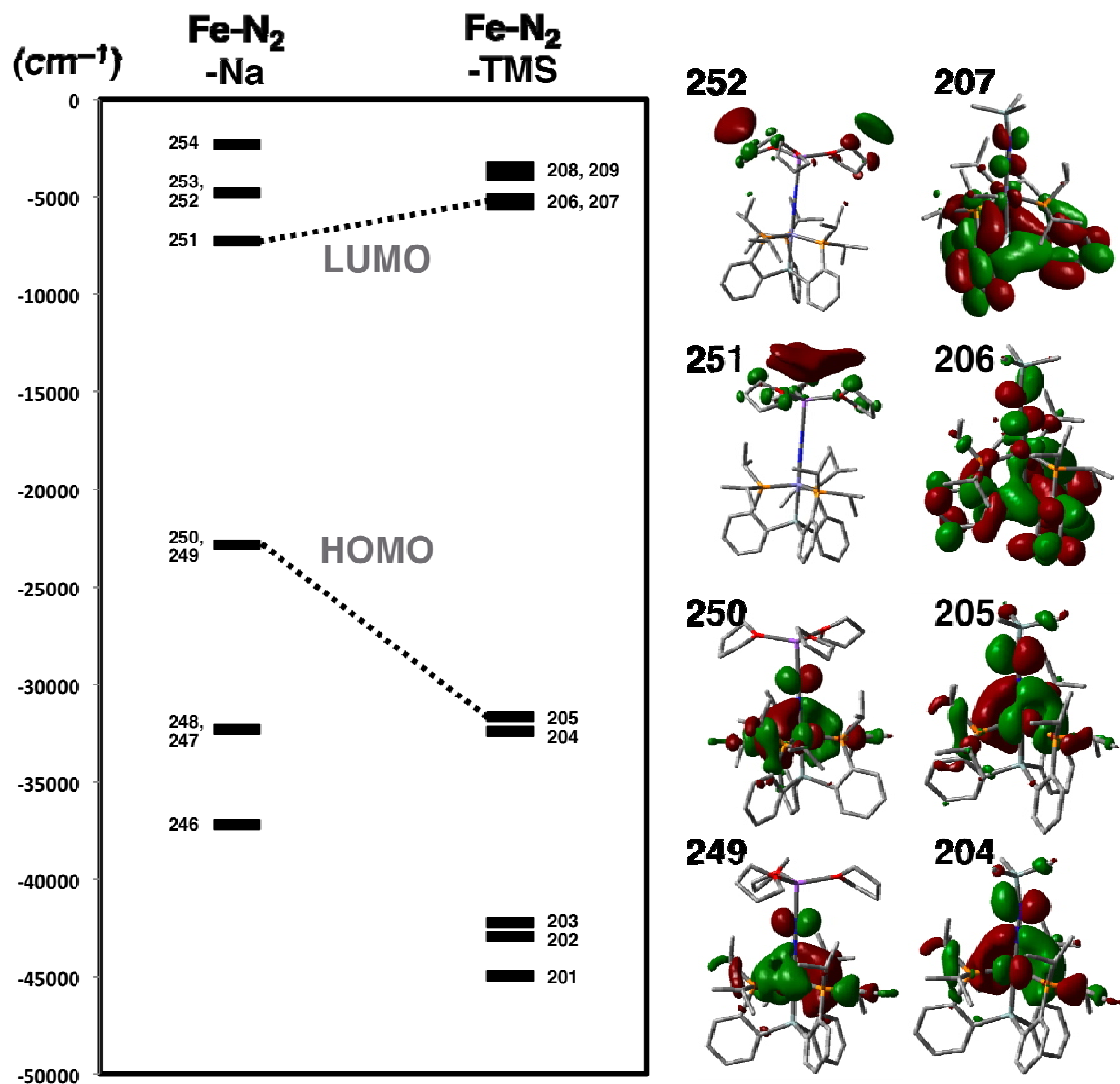
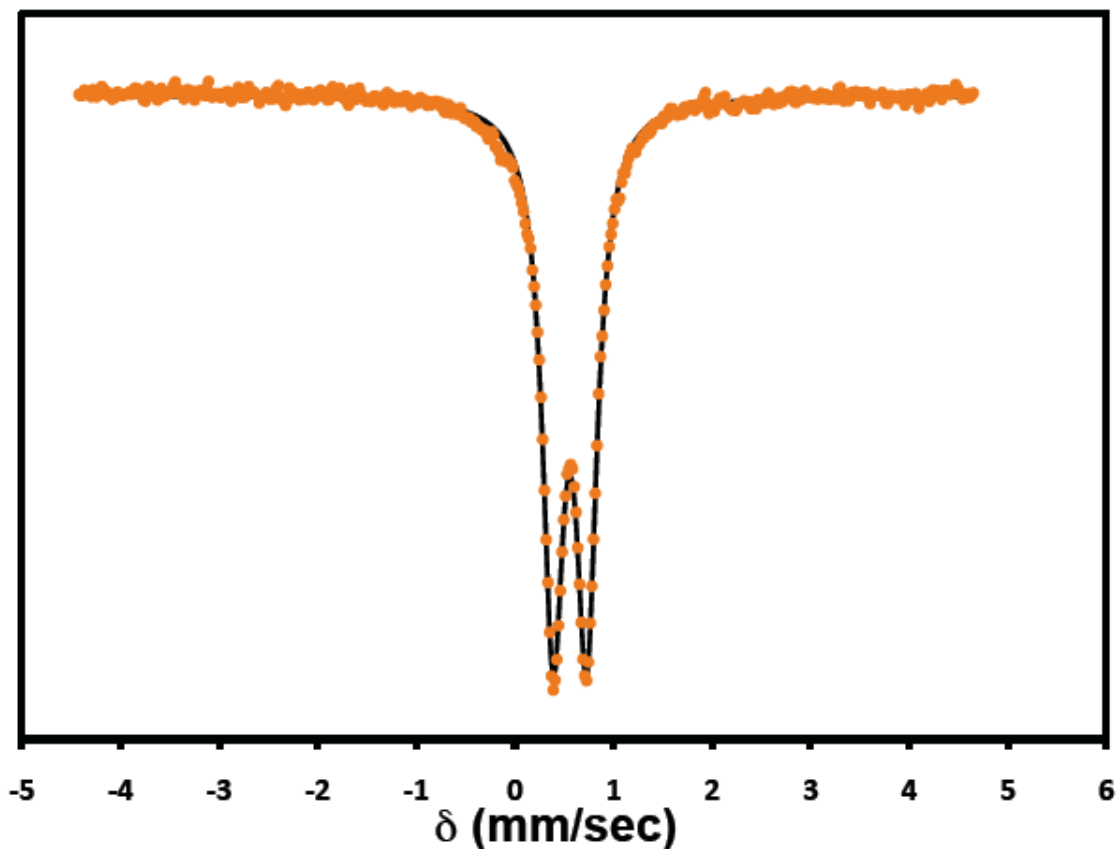


Figure S53. Molecular orbital diagrams for **5** and **12** from the single point DFT calculations (left). Selected molecular orbitals for LUMOs and HOMOs are depicted (right).



**Figure S54.** Zero field Mössbauer spectrum of  $(\text{SiP}^{i\text{Pr}}_3)\text{Fe}(\text{Cl})$  recorded at 77 K. The dotted lines are the experimental data and the solid lines are fits using the parameters listed in Table 2.





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- <sup>iii</sup> Brookhart, M., Grant, B. & Volpe, Jr, A. F.  $[(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4\text{B}]^-\text{[H(OEt}_2)_2]^+$ : a convenient reagent for generation and stabilization of cationic, highly electrophilic organometallic complexes. *Organometallics* **11**, 3920-3922 (1992).
- <sup>iv</sup> Sheldrick, G. M. A short history of *SHELX Acta Cryst. A* **64**, 112 (2008).
- <sup>v</sup> Evans, D. F. The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance. *J. Chem. Soc.*, 2003-2005 (1959).
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- <sup>vii</sup> Frisch, M. J., et al. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford, CT, (2004).
- <sup>viii</sup>  $\tau = 0.00$  for a perfect square pyramid (SP) and  $\tau = 1.00$  for a trigonal bipyramidal (TBP) geometry. See for example: Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. Synthesis, Structure and Spectroscopic Properties of Copper(II) Compounds Containing Nitrogen-Sulfur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) Perchlorate. *J. Chem. Soc. Dalton Trans.* 1349-1356 (1984).
- <sup>ix</sup> Frisch, M. J., et al. The reduction of  $[\text{Fe}(\text{CO})_2\text{L}_2\text{X}_2]$  ( $\text{L} = \text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OiPr})_3$ ,  $\text{PEt}_3$ ;  $\text{X} = \text{Br}$ ,  $\text{I}$ ) – From iron(II) to iron(0) via stable iron(I) intermediates. *Chem. Eur. J.* **1**, 541-548 (1995).
- <sup>x</sup> Betley, T. A. and Peters, J. C. A tetrahedrally coordinated  $\text{L}_3\text{Fe-N}_x$  Platform that accommodates terminal nitride ( $\text{Fe}^{\text{IV}}\equiv\text{N}$ ) and dinitrogen ( $\text{Fe}^{\text{I}}\text{-N}_2\text{-Fe}^{\text{I}}$ ) ligands. *J. Chem. Soc.*, 6252-6254 (2004).



- <sup>xi</sup> The initial red solution (30 min) was taken out and dried after washing with pentane to eliminate excess phenylhydrazine. <sup>1</sup>H-NMR and IR data of the red species reveal it to be the phenylhydrazine adduct [(SiP<sup>Ph</sup><sub>3</sub>)Fe(N<sub>2</sub>H<sub>3</sub>C<sub>6</sub>H<sub>5</sub>)] [B(3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 13.3, 8.7, 8.6, 8.1, 7.7, 4.9, -4.1, -5.6. IR (KBr; cm<sup>-1</sup>): 3346, 3271, 3203. The hydrazine product was slowly converted to the ammonia adduct **5a** by storing the NMR tube at RT overnight, or by heating it at 60 °C for 2 hrs. The reaction was monitored by <sup>1</sup>H-NMR.
- <sup>xii</sup> Trace amount of **4b** can be seen from <sup>1</sup>H-NMR. Currently, we were not able to quantify the amount of impurity.
- <sup>xiii</sup> Whited, M. T., Mankad, N. P., Lee, Y., Oblad, P. F. & Peters, J. C. Dinitrogen Complexes Supported by Tris(phosphino)silyl Ligands. *Inorg. Chem.* **48**, 2507-2517 (2009).